SOVIET PHYSICS JETP VOLUME 33, NUMBER 4 OCTOBER, 1971

EFFECTIVENESS OF THE EXCITON MECHANISM OF SUPERCONDUCTIVITY IN LAYERED COMPOUNDS WITH MOLECULES

L. N. BULAEVSKIĬ and Yu. A. KUKHARENKO

P. N. Lebedev Physics Institute, USSR Academy of Sciences

Submitted November 9, 1970

Zh. Eksp. Teor. Fiz. 60, 1518–1524 (April, 1971)

We consider the interaction of electrons in layered compounds consisting of conducting layers of dichalcogenides and non-conducting molecular layers with van der Waals interaction of the molecules with one another and with the layers of the dichalcogenides (compounds of the type TaS_2 (pyridine) $\frac{1}{2}$). It is shown that in such systems the contribution of the exciton mechanism to the effective attraction of the conduction electrons is small compared with phonon contribution, and the temperature of the superconducting transition is determined by the phonon mechanism. In compounds of the layered type, the exciton mechanism of the superconductivity can be effective only in those cases when the excitons of the non-conducting layers have a low ($\approx$0.1–1 eV) energy as the result of strong delocalization (for example, in a system of alternating conducting and semiconducting layers).

By now there have been synthesized layered compounds of the type TaS_2 (pyridine) $\frac{1}{2}$[1], with which it is hoped to obtain high-temperature superconductors with the exciton mechanism of superconductivity[2,3]. In these compounds, conducting flat layers of dichalcogenides (TaS_2, $NbSe_2$, etc.) alternate with planes of pyridine molecules (C_5H_5N), with the TaS_2 layers and the pyridine molecules bound in the crystal by van der Waals forces.

In such crystals, the pyridine can be replaced by another molecule with excitation energy $\Omega \sim 0.1-1$ eV, sufficiently low for logarithmic cutoff of the Coulomb repulsion of the conducting electrons[3,4] (it is necessary that Ω be small compared with the Fermi energy of the conduction electrons ϵ_F and with the plasmon energy ω_0; for pyridine, $\Omega \approx 5$ eV, and there are no grounds for expecting the exciton mechanism to be effective). If the effective interaction of the electrons due to the exchange of excitons can be made sufficiently strong, then we have at our disposal the parameter Ω, variation of which can yield values of the superconducting-transition temperature T_c which are maximal for the system of the conduction electrons of the dichalcogenide layers.

The purpose of the present work was an investigation of two questions: 1) the extent to which thermodynamic fluctuations in such an almost-two-dimensional system can influence the value of T_c; 2) the extent to which it is possible to make effective the interaction of the conducting electrons by exciton exchange (compared with phonon exchange).

1. In the compounds investigated in[1], the molecular excitons are strongly localized (the width of the exciton band is much smaller than the exciton energy), owing to the van der Waals character of the interaction of the molecules. In this case the excitation energy $\Omega \sim 0.1-1$ eV can be realized only in large molecules, for example, in planar molecules with $N \gtrsim 30$ π electrons in the conjugation chain and with linear dimensions $l \gtrsim 9$ Å. When such molecules are introduced into the crystal, the layers of the dichalcogenides will be pushed apart to a distance exceeding 18 Å. In[1] it was shown experimentally that when the conducting layers are moved from 12 to 18 Å apart (one and two pyridine layers between the dichalcogenide layers, respectively), the transition temperature T_c changes insignificantly. We can therefore expect the critical temperature not to be greatly lowered by the thermodynamic fluctuations when the pyridine is replaced by large molecules.

Following Dzyaloshinskiĭ and Kats[5], it can be assumed that the weak dependence of T_c on the number of pyridine layers between the conducting layers is connected with the weak logarithmic dependence of T_c on the anisotropy parameter α (this parameter shows the extent to which transitions of electrons inside the conducting layers are more probable than transitions between layers). Indeed, the role of the thermodynamic fluctuations in the lowering of the temperature of the transition can be estimated with the aid of the correlation function $\langle \psi^*(\mathbf{r})\psi(0) \rangle$ of the Ginzburg-Landau ordering parameter. For the three-dimensional isotropic case we obtained for it in[6] the following asymptotic expression at large r:

$$\langle\psi^*(\mathbf{r})\psi(0)\rangle \sim \psi_0^2 \exp\left\{-\frac{T}{4c\psi_0^2}\frac{1}{V}\sum_{\mathbf{k}}^{k<Q}\frac{2(1-\cos\mathbf{kr})}{k^2}\right\}. \qquad (1)$$

Here ψ_0 is the modulus of the ordering parameter, Q the maximum momentum, V the volume of the system, and c a coefficient with which the square of the modulus of the gradient of the ordering parameter enters in the Ginzburg-Landau expansion for the free energy. In writing down (1) we neglected the fluctuations of the modulus of the ordering parameter, which are immaterial for our purposes. On the basis of (1) it can be shown that in the three-dimensional isotropic case the fluctuations of the phase of the ordering parameter are significant only in the vicinity of the transition point $\tau = |T - T_c|/T_c \sim mQT_c/\pi^2\hbar^2 n \sim 10^{-7}$ (m—electron mass, n—electron density). In an anisotropic system, the factor $1/ck^2$ in the argument of the exponential in formula (1) should be replaced by $1/\epsilon(k, q)$, where $\epsilon(k, q) \approx \hbar^2(k^2 + \alpha q^2)/2m$ is the energy of an electron with momentum k lying in the plane of the layers and momentum q connected with the motion of the electron between the layers. In this case $\tau \sim mQT_c|\ln\alpha|/\pi^2\hbar^2 n$, where $Q = \max(q)$. When $Q < 10^7\ \mathrm{cm}^{-1}$ we have $\tau \lesssim 10^4|\ln\alpha|$. Therefore the transition temperature T_c obtained with allowance for the fluctuations may differ from the temperature T_{c0} calculated without allowance for the phase fluctuations only by a quantity on the order of τT_{c0} (the fluctuations of the modulus of the ordering parameter remain finite as $\alpha \to 0$, and, as stated above, they can be disregarded). Therefore when $\tau \ll 1$ and $\epsilon_F\alpha \ll T_{c0}$ we deal with quasi-two-dimensional superconductivity[5], when T_c can be calculated by the usual method of the self-consistent field[7], by putting $\alpha = 0$.

2. Kirzhnits, Maksimov, and Khomskiĭ[4] (see also[3]) have shown that the exciton mechanism in an isotropic three-dimensional crystal can be effective only in the case when the interaction of the conduction electrons $V_{ex}(0, 2k_F)$ via the excitons at zero energy transfer and large momentum transfers (on the order of $2k_F$) is no weaker than the analogous interaction via the phonon system ($V_{ph}(0, 2k_F)$). Only when $\delta = V_{ex}(0, 2k_F)/V_{ph}(0, 2k_F) \gtrsim 1$, does the quantity T_c depend strongly on Ω and only then can it be increased by introducing into the system excitons with $\Omega \gg \omega_D$ (ω_D is the Debye energy of the phonon).

Let us consider systems consisting of alternating molecular and conducting layers, in which the interaction of the molecules with one another and with the conducting layers of the dichalcogenides is of the van der Waals type. We shall show that in such systems the quantity δ is small because of the spatial separation of the conduction electrons and the molecular electrons, and also because of the large size of the molecules necessary to realize sufficiently low frequencies Ω.

Let us calculate the contribution of the excitons to the effective interaction of the conduction electrons in layered compounds of the type indicated above. As a model of these compounds we take a system of alternating infinitesimally thin conducting planes and molecular layers with distance R between them ($R \approx 3$ Å).

Let us consider first the case when the molecules have the form of squares (with sides l), and their planes, which we also assume to be infinitesimally thin, are parallel to the conducting planes. If we neglect the effects of periodicity of the lattice, then the system can be regarded as homogeneous in the plane of the layers (x, y). The coordinates of the planes are determined by the expression $z_n = Rn$, where n are integers, with even n corresponding, for example, to the conducting planes, and odd ones to the molecular planes. In accordance with the statement made above concerning the quasi-two-dimensional character of the superconductivity, we can disregard the fluctuations in the zeroth approximation and use the equations of the self-consistent field, putting in them $\alpha = 0$. We shall therefore disregard the overlap of the wave functions of the conduction electrons with the wave functions of the molecular electrons, i.e., the motion of the conducting electrons will be assumed to be two-dimensional. In the random-phase approximation, the effective interaction of the electrons is determined by the equation[8]

$$\begin{gathered} V(\omega, \mathbf{k}, n, n') = V_0(\mathbf{k}, n-n') \\ -\sum_m \Pi_m(\omega, \mathbf{k}) V_0(\mathbf{k}, n-m) V(\omega, \mathbf{k}, m, n'), \\ V_0(\mathbf{k}, n-n') = 2\pi k^{-1} \exp\{-kR|n-n'|\}, \end{gathered} \tag{2}$$

where $V(\omega, \mathbf{k}, n, n')$ is the Fourier component of the effective interaction $V(\omega, \mathbf{r}, n, n')$ with respect to the coordinates $\mathbf{r}(x, y)$, $V_0(\mathbf{k}, n - n')$ is the Fourier component of the Coulomb interaction of the electrons in the layers n and n′, and $\Pi_m(\omega, \mathbf{k})$ is the polarization operator of the plane m:

$$\begin{gathered} \Pi_{2n}(\omega, \mathbf{k}) = \Pi_1(\omega, \mathbf{k}), \\ \Pi_{2n+1}(\omega, \mathbf{k}) = \Pi_2(\omega, \mathbf{k}). \end{gathered} \tag{3}$$

For conducting layers at small ω ($\omega \ll \epsilon_F$), we have

$$\Pi_1(0, \mathbf{k}) = \begin{cases} a_0^{-1}, & k \leqslant 2k_F, \\ a_0^{-1}\left[1 - \sqrt{1-(2k_F k^{-1})^2}\right], & k > 2k_F, \end{cases} \tag{4}$$

where a_0 is the Bohr radius of the conduction electrons and k_F is the Fermi momentum, $k_F = \sqrt{2\pi n_1}$, where n_1 is the surface density of the conduction electrons.

For the molecular planes

$$\Pi_2(\omega, \mathbf{k}) = e^2 n_2 \left[\frac{1}{\Omega - \omega - i\delta} + \frac{1}{\Omega + \omega + i\delta}\right] \xi(\mathbf{k}). \tag{5}$$

$$\xi(\mathbf{k}) = |\langle 0|e^{i\mathbf{kr}}|f\rangle|^2,$$

where n_2 is the surface density of the molecules and $\Pi_2(\omega, \mathbf{k})$ takes into account the contribution of only one lower excited state f, the transition to which from the ground state is strong. In (5) we have neglected effects connected with the delocalization of the excitons, assuming the interaction of the molecules in the layer to be of the van der Waals type, and the matrix element of the operator $\exp(i\mathbf{k}\cdot\mathbf{r})$ is calculated from the wave functions of the ground state of the molecule and its excited state f. We note that the real structure, of course, is not homogeneous in the (x, y) plane and that in the coordinate space the polarization operator depends on the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$, and not on their difference. The operator $\Pi_2(\omega, \mathbf{r}_1 - \mathbf{r}_2)$, the Fourier component of which with respect to $\mathbf{r}_1 - \mathbf{r}_2$ is determined by expression (5), is obtained from $\Pi_2(\omega, \mathbf{r}_1 - \mathbf{r}_2)$ by averaging over $(\mathbf{r}_1 + \mathbf{r}_2)/2$, and it thus determines the polarization of the molecules averaged over the plane.

The structure under consideration is periodic in the coordinate z with a period 2R, and therefore the quantities $V_{11}(\omega, \mathbf{k}, n, n') \equiv V(\omega, \mathbf{k}, 2n, 2n')$ and $(V_{12}(\omega, \mathbf{k}, n, n') \equiv V(\omega, \mathbf{k}, 2n, 2n'+1)$ depend only on $n - n'$. Going over to the Fourier representation $\tilde{V}_{11}(\omega, \mathbf{k}, q)$, $\tilde{V}_{12}(\omega, \mathbf{k}, q)$ with respect to the discrete variable $n - n'$, we obtain

$$\tilde{V}_{11}(\omega, \mathbf{k}, q) = \frac{2\pi}{k}\,\mathrm{th}\,kR\,\frac{P_1(\omega, \mathbf{k})}{P_1(\omega, \mathbf{k})P_2(\omega, \mathbf{k}) - \cos^2 q\,\mathrm{ch}^{-2}kR}, \tag{6}$$

$$P_{1,2}(\omega, \mathbf{k}) = 1 + 2\pi k^{-1}\,\mathrm{th}(kR)\,\Pi_{1,2}(\omega, \mathbf{k}).$$

We note that the effective interaction of the conduction electrons can be written with the aid of the dielectric constant $\epsilon(\omega, \mathbf{k}, q)$:

$$\tilde{V}_{11}(\omega, \mathbf{k}, q) = \frac{\tilde{V}_0(\mathbf{k}, q)}{\varepsilon(\omega, \mathbf{k}, q)}, \quad \tilde{V}_0(\mathbf{k}, q) = \frac{2\pi}{k} \frac{\operatorname{th} kR}{1 - \cos^2 q \operatorname{ch}^{-2} kR},$$

$$\varepsilon(\omega, \mathbf{k}, q) = 1 + \frac{2\pi}{k} \frac{\operatorname{th} kR}{1 - \cos^2 q \operatorname{ch}^{-2} kR}$$

$$\times \left[\Pi_1(\omega, \mathbf{k}) + \frac{\Pi_2(\omega, \mathbf{k}) \cos^2 q \operatorname{ch}^{-2} kR}{1 + 2\pi k^{-1} \operatorname{th}(kR) \Pi_2(\omega, \mathbf{k})}\right]. \tag{7}$$

The effective interaction of the electrons inside the plane is determined by the expression

$$V(\omega, \mathbf{k}, 0) = \int_0^{2\pi} \frac{dq}{2\pi} \tilde{V}_{11}(\omega, \mathbf{k}, q) = \frac{2\pi}{k} \operatorname{sh} 2kR \cdot$$

$$\times \frac{P_2(\omega, \mathbf{k})}{\{[2\operatorname{ch}^2(kR) P_1(\omega, \mathbf{k}) P_2(\omega, \mathbf{k}) - 1]^2 - 1\}^{1/2}}, \tag{8}$$

which can also be written in the form

$$V(\omega, \mathbf{k}, 0) = \frac{V_0(\mathbf{k}, 0)}{\varepsilon(\omega, \mathbf{k})}, \quad V_0(\mathbf{k}, 0) = \frac{2\pi}{k},$$

$$\varepsilon(\omega, \mathbf{k}) = \frac{\{[2 \operatorname{ch}^2(kR) P_1(\omega, \mathbf{k}) P_2(\omega, \mathbf{k}) - 1]^2 - 1\}^{1/2}}{\operatorname{sh}(2kR) P_2(\omega, \mathbf{k})}. \tag{9}$$

3. We note first that in the system under consideration there is screening—the effective interaction of the electrons decreases exponentially with increasing distance between them (the role of this screening in the appearance of phase fluctuations was discussed in[5]). However, unlike ordinary metals, in a layered system the screening is strongly anisotropic. Thus, without allowance for the molecule polarization ($\Pi_2 = 0$) we obtain for the effective interaction of the electrons inside the layer, when $\omega = 0$, $4k_F R > \pi$, $R \gg a_0$ for large r and $z = 0$:

$$V_{11}(0, r, 0) \approx 4\pi \left(\frac{R}{a_0}\right)^{3/2} \frac{1}{r} \exp\left\{-\frac{\pi r}{2R}\right\}. \tag{10}$$

The interaction between the planes, for $z \gg 2R$ and $r = 0$, is determined by the expression

$$V_{11}(0, 0, z) \approx \frac{3a_0}{2Rz} \exp\left\{-\frac{z}{2R} \ln \frac{4R}{a_0}\right\}. \tag{11}$$

Thus, when $R \gg a_0$ the screening inside the plane is weaker than the screening between planes.

We now proceed to a comparative estimate of the exciton and phonon contributions to the effective interaction of the electrons at $\omega = 0$. The contribution of the exciton mechanism in (8) is obtained by subtracting from $V(\omega, \mathbf{k}, 0)$ the Coulomb part of the effective interaction of the conducting electrons $V_C(\omega, \mathbf{k}, 0)$ which is equal to $V(\omega, \mathbf{k}, 0)$ at $\Pi_2 = 0$. The contribution of the phonon mechanism at $\omega = 0$ coincides in order of magnitude with $V_C(0, \mathbf{k}, 0)$, and thus

$$\delta(k) = \frac{V_{ex}(0, k, 0)}{V_{ph}(0, k, 0)} = \frac{V(0, k, 0)}{V_c(0, k, 0)} - 1. \tag{12}$$

Substituting the expressions (4), (5), and (8) in (12), we obtain

$$\delta(k) < \frac{1}{2} \operatorname{ch}^{-2} kR \frac{\Pi_2(0, k)}{\Pi_1(0, k)} = \frac{2\pi e^2 n_2 a_0}{\Omega} \xi(k) \operatorname{ch}^{-2} kR. \tag{13}$$

With allowance for $\Omega \approx e^2/a_0 N$ (N is the number of π electrons in the molecule) and $n_2 \approx 1/9\, a_0^2 N$, we can write (13) in the form

$$\delta(k) < \xi(k) \operatorname{ch}^{-2} kR < 1. \tag{14}$$

The factor $\cosh^{-2} kR$ cuts off the exciton part of the effective interaction at momentum transfers $k > 1/R$. Its origin is physically understandable—the conduction electrons and the molecular electrons are removed from one another by a distance R and the transfer of momenta larger than $1/R$ is impossible. Thus, this factor is due to the van der Waals character of the interaction of the layers and is organically connected with the structure of the layered compounds.

Let us now consider the factor $\xi(k)$. To estimate it in order of magnitude, we assume for the molecule a model of a two-dimensional square well with infinite walls and with width $l \approx 3a_0\sqrt{N}$, in which N electrons move. Then the single-electron wave functions and the electron energies are given by

$$\psi_{k_1, k_2}(x, y) = \frac{2}{l} \sin k_1 x \sin k_2 y, \quad k_{1,2} = \frac{\pi m_{1,2}}{l},$$
$$\varepsilon_{k_1, k_2} = \hbar^2 (k_1^2 + k_2^2) / 2m, \quad 0 \leqslant x,\ y \leqslant l, \tag{15}$$

where m_1 and m_2 are integers. The lower excitation frequency $\Omega \approx e^2/a_0 N$ can be obtained for electron transitions with changes of both quantum numbers m_1 and m_2 (when the change of $m_1^2 + m_2^2$ is of the order of unity about the values m_1 and $m_2 \sim \sqrt{N}/2$). In such transitions we have

$$\xi(k) \approx \left(\frac{2}{l} \int_0^l \sin k_1 x \sin k_1' x \cos kx dx\right)^4 \lessapprox \begin{cases} (kl)^8, & kl \leqslant 1, \\ (kl)^{-4}, & kl \gg 1. \end{cases} \tag{16}$$

From (16) we see that the factor $\xi(k)$ cuts off the effective interaction of the electrons via the molecules at momentum transfers on the order of $1/l$. Its physical meaning is likewise clear—a molecule with linear dimensions l cannot be effectively acted upon by an external field with a wavelength smaller than l. For the structures in question, the factor $\xi(k)$ is decisive, since $l \gg R$.

The contribution of the excitons to the pairing interaction which determines T_C is determined in the isotropic three-dimensional case by the quantity

$$\overline{V}_{ex} = \int_0^{2k_F} V_{ex}(0, k) \frac{k}{2k_F} dk, \tag{17}$$

where $\overline{V}_{ex}$ is the value of $V_{ex}(0, k)$ averaged over the angles, and integrated over all the momentum transfers k (for details see[3,4]). Analogously, in the quasi-two-dimensional crystal the contribution of the exciton mechanism is also determined by the quantity

$$\overline{V}_{ex} = \frac{2}{\pi} \int_0^{2k_F} V_{ex}(0, k) (4k_F^2 - k^2)^{-1/2} dk. \tag{18}$$

Taking (12) and (14) into account, we have

$$\overline{V}_{ex} = \frac{2}{\pi} \int_0^{2k_F} \delta(k) V_{ph}(0, k) (4k_F^2 - k^2)^{-1/2} dk \lessapprox$$

$$\lessapprox \frac{2}{\pi} \int_0^{2k_F} V_{ph}(0, k) (4k_F^2 - k^2)^{-1/2} dk \cdot \frac{1}{2k_F} \int_0^{2k_F} \delta(k) dk = (2k_F l)^{-1} \overline{V}_{ph}. \tag{19}$$

The quantity $(2k_F l)^{-1}$ does not exceed 0.03 when $\Omega < 1$ eV and at average distances a between the electrons and the conducting plane on the order of 1.5 Å.

Analogous calculations for the structure with molecules lying in the layer in such a way that their planes are perpendicular to the conducting planes leads to an expression for $\delta(k)$ that differs from (13) and (14) by a factor $R^{-1} l$, for in this case the distance between the planes of the molecules in the layer is of the order of

R and $n_2 \approx (lR)^{-1}$. In such a system the difference between the exciton contribution and the phonon contribution is determined at least by the factor $(2k_FR)^{-1} \approx 0.1$ and the exciton mechanism is likewise ineffective.

We note that introduction of linear molecules such as polyenes in the space between the conducting layers of the dichalcogenides, with the polyenes placed perpendicular to the conducting layers, would increase n_2 to R^{-2}. However, for linear molecules of any length we have $\Omega > 2.2$ eV (see, for example,[9]) and this value of Ω is apparently not small enough for an effective cutoff of the Coulomb repulsion of the conduction electrons.

Thus, in the case of layered compounds with molecular excitons we are unable to make the exciton mechanism effective, owing to the factor $\xi(k)$ in (5), which cuts off the interaction via the excitons at momentum transfers $k \lesssim l^{-1} \ll 2k_F$. This result is connected with the large linear dimensions of the molecules—the inevitable price that must be paid for the low excitation energies of the localized molecular excitons1). In principle, however, lower exciton energies can be obtained as a result of their strong delocalization (by replacing, for example, layers with weakly interacting molecules by semiconducting layers). In systems with delocalized excitons it is apparently possible to obtain $\xi(k) \approx 1$ at large k, but the factor of the type $\cosh^{-1}kR$ does remain. One can hope to compensate for the associated decrease of $\overline{V}_{ex}$ by increasing $V_{ex}(0, k)$ for $k \lesssim 1/R$.

Thus, from the point of view of using the exciton mechanism of superconductivity, interest attaches to the synthesis and experimental investigation of layered compounds consisting of alternating conducting layers of dichalcogenides and semiconducting layers.

In conclusion, the authors are deeply grateful to V. L. Ginzburg and the participants of the seminar under his direction for a discussion of the work and for valuable remarks.

---

1) In other words, the oscillator strength for an exciton with low frequency and large quasimomenta on the order of $2k_F$ is not large enough in the dielectric constant of layered compounds with molecules. This result is closely connected with the localized character of the molecular excitons.

---

[1] F. R. Gamble, F. J. Salov, R. A. Klemm, and T. H. Geballe, Science, **168**, N 3931, 568 (1970).

[2] W. A. Little, Phys. Rev., **134A**, 1416 (1964).

[3] V. L. Ginzburg, Usp. Fiz. Nauk **101**, 185 (1970) [Sov. Phys.-Usp. **13**, 335 (1970)]; Cont. Phys., **9**, 355 (1968).

[4] D. A. Kirzhnits, E. G. Maksimov, and D. I. Khomskiĭ, FIAN Preprint No. 108, (1970).

[5] I. E. Dzyaloshinskiĭ and E. I. Kats, Zh. Eksp. Teor. Fiz. **55**, 338 (1968) [Sov. Phys.-JETP **28**, 178 (1969)].

[6] T. M. Rice, Phys. Rev., **140A**, 1889 (1965).

[7] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, 1962.

[8] D. A. Kirzhnits, Polevye metody teorii mnogikh chastits (Field Methods of Many-Particle Theory), Gosatomizdat, 1963.

[9] M. J. Dewar, J. Chem. Soc., September, 3532, 1952.

Translated by J. G. Adashko
166