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

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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) $\frac{1}{2}$, with which it is hoped to obtain high-temperature superconductors with the exciton mechanism of superconductivity (1, 2, 3). In these compounds, conducting flat layers of dichalcogenides (TaS$_2$, NbSe$_2$, etc.) alternate with planes of pyridine molecules (C$_5$H$_5$N), 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 (4, 5, 6) (it is necessary that $\Omega$ be small compared with the Fermi energy of the conduction electrons $\epsilon_F$ and with the plasmon energy $\omega_{pl}$ 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 $\Omega$, 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 $N \approx 30$ $\pi$ electrons in the conjugation chain and with linear dimensions $t \gtrsim 5$ 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 Dzyaloshinskii and Kat$^1$, 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 $\alpha$ (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 $\langle \phi^*(r)\phi(0) \rangle$ of the Ginzburg-Landau ordering parameter. For the three-dimensional isotropic case we obtained for it in (3) the following asymptotic expression at large $r$:

\[ \langle \phi^*(r)\phi(0) \rangle \sim \psi_0^4 \exp \left( -\frac{T}{4c\psi_0^2} \frac{1}{V} \sum_{k} 2(1 - \cos kr) \right). \]  

Here $\psi_0$ 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 $\tau = |T - T_c|/T_c \sim mQ^4T_c/e^4\hbar^2n \sim 10^{-7}$ (m-electron mass, $n$-electron density). In an anisotropic system, the factor $1/c^2$ in the argument of the exponential in formula (1) should be replaced by $1/e(k, q)$, where $e(k, q) = \hbar^2(k^2 + aq^2)/2m$ 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 \( \tau \sim \frac{m Q T_C}{|\alpha|/\pi^2 h^2 n} \), where \( Q = \max (q) \). When \( Q < 10^7 \text{cm}^{-2} \) we have \( \tau \lesssim 10^4 / |\alpha| \). 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 \( T_{C0} \), 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 \( \epsilon \sigma_T \ll \tau_{C0} \) 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 Khomskii\(^{(4)} \) (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 \( V_{\text{ex}}(0, 2k_F) \) via the excitons at zero energy transfer and large momentum transfers (on the order of \( 2k_F \)) is no weaker than the analoguous interaction via the phonon system \( (V_{\text{ph}}(0, 2k_F)) \). Only when \( \delta = V_{\text{ex}}(0, 2k_F)/V_{\text{ph}}(0, 2k_F) \geq 1 \), does the quantity \( T_C \) depend strongly on \( \Omega \) and only then can it be increased by introducing into the system excitons with \( \Omega \gg \omega_D \) (\( \omega_D \) 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 \( \delta \) 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 \( \Omega \).

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 \((R \approx 3 \AA)\).

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 \( z_n = R_n \), 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\(^{(8)} \):

\[
V(\omega, k, n, n') = \frac{2\pi}{k} \frac{P_{\omega}(k)}{P_{\omega}(k)} \frac{1}{\epsilon_{\omega}(k)} \frac{1}{\epsilon_{\omega}(k')} \left[ \frac{1}{\omega_D} \right]^{1/2} P_{\omega}(k) P_{\omega}(k') \cos \theta \exp \{-ikR - i\theta_{R}\}.
\]

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

\[
V(\omega, k, n, n') = \frac{2\pi}{k} \frac{P_{\omega}(k)}{P_{\omega}(k)} \frac{1}{\epsilon_{\omega}(k)} \frac{1}{\epsilon_{\omega}(k')} \left[ \frac{1}{\omega_D} \right]^{1/2} P_{\omega}(k) P_{\omega}(k') \cos \theta \exp \{-ikR - i\theta_{R}\}.
\]
\[ V_r(0, \mathbf{q}, \mathbf{k}) = \frac{V_x(k, q)}{\epsilon(\mathbf{q}, \mathbf{k})}, \quad \epsilon(\mathbf{q}, \mathbf{k}) = \frac{2\pi}{k} \frac{\text{th} kr}{1 - \cos q \text{ch}^{-1} kr}, \]

which can also be written in the form

\[ \epsilon(\mathbf{q}, \mathbf{k}) = \frac{2\pi}{k} \frac{\text{th} kr}{1 - \cos q \text{ch}^{-1} kr} \times \left[ \frac{2\pi}{k} \frac{\text{th} (kr) \Pi(\mathbf{q}, \mathbf{k})}{1 + 2\pi \text{th}(kr) \Pi(\mathbf{q}, \mathbf{k})} \right]. \]

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

\[ V(\mathbf{q}, \mathbf{k}) = \frac{\text{th} kr}{2\pi} \frac{\epsilon(\mathbf{q}, \mathbf{k})}{\epsilon(\mathbf{q}, \mathbf{k})} \times \frac{\text{th} (kr) \Pi(\mathbf{q}, \mathbf{k})}{1 + 2\pi \text{th}(kr) \Pi(\mathbf{q}, \mathbf{k})} \]

which can also be written in the form

\[ V(\mathbf{q}, \mathbf{k}) = \frac{\text{th} kr}{2\pi} \frac{\epsilon(\mathbf{q}, \mathbf{k})}{\epsilon(\mathbf{q}, \mathbf{k})} \times \frac{\text{th} (kr) \Pi(\mathbf{q}, \mathbf{k})}{1 + 2\pi \text{th}(kr) \Pi(\mathbf{q}, \mathbf{k})} \]

The interaction of the electrons at the interaction of the conducting electrons 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 \( \omega = 0 \), \( 4k_F r > R \), \( R > a_0 \) for large \( r \) and \( z = 0 \):

\[ V_n(0, r, 0) \approx 4\pi \left( \frac{R}{a_0} \right) \ln \frac{r}{2R} \exp \left( -\frac{r}{2R} \right). \]

The interaction between the planes, for \( z > 2R \) and \( r = 0 \), is determined by the expression

\[ V_n(0, 0, z) \approx 3\pi \frac{\epsilon(\mathbf{q}, \mathbf{k})}{2R} \exp \left( -\frac{z}{2R} \ln \frac{4R}{a_0} \right). \]

Thus, when \( R > a_0 \) 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 \( V_C(\omega, \mathbf{k}, 0) \), and thus

\[ \delta(k) = \frac{\epsilon(\mathbf{q}, \mathbf{k})}{\epsilon(\mathbf{q}, \mathbf{k})} \times \frac{\text{th} (kr) \Pi(\mathbf{q}, \mathbf{k})}{1 + 2\pi \text{th}(kr) \Pi(\mathbf{q}, \mathbf{k})}. \]

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

\[ \delta(k) = \frac{1}{2} \text{ch}^{-2} kr \left( \frac{\Pi_2(\mathbf{q}, \mathbf{k})}{\Pi_0(\mathbf{q}, \mathbf{k})} \right)^2 \text{ch}^{-1} kr. \]

With allowance for \( \Omega \approx e^2/a_0N \) (\( N \) is the number of \( n \) electrons in the molecule) and \( a_0 \approx 1/9a_0N \), we can write (13) in the form

\[ \delta(k) = \xi(k) \text{ch}^{-2} kr \approx 1. \]

The factor \( \text{ch}^{-2} kr \) cuts off the exciton part of the effective interaction at momentum transfers \( k < 1/R \).
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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.

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

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