Possible mechanism of high-temperature superconductivity

A. A. Abrikosov

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences
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A superconductivity mechanism based on the formation of "metallic excitonium", the exciton phase in a semiconductor or in a semimetal with $m_e/m_a \lesssim 0.01$, is proposed.

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Recent experiments by Brandt, Kuvshinnikov Rusakov, and Semenov[1] have reawakened interest in the possibility of high-temperature superconductivity. A mechanism explaining the almost complete Meissner effect observed in[1] was proposed in[2]. This explanation is based on the idea of a transition to a new excitonic phase characterized by the presence of a spontaneous current.

In this article we call attention to one principally rather simple mechanism of producing high-temperature superconductivity, which is possibly realized in CuCl at high pressures.

Halperin and Rice, in their well known article,[3] have analyzed various types of excitonic phases and, in particular, have noted C. Herring's idea that "crystalline excitonium" can be created at a large mass difference between the electrons and holes. If the spectra of the electrons and holes are isotropic, then an individual exciton is in this case quite similar to a hydrogen atom, so that one can imagine that condensed phases of these excitons are just like those of hydrogen—molecular liquid, molecular crystal, atomic crystal (metallic hydrogen). Of course, the characteristic parameters of these phases will be different than those of hydrogen: the role of the atomic dimensions will be played by $r_B^* = \epsilon_0/m_e e^2$ (we use $\hbar = 1$ throughout), where ϵ_0 is the dielectric constant and m_e is the effective mass of the electron (we assume that $m_e \ll m_h$). In addition to ordinary sound, exciton-lattice vibrations will exist and the corresponding vibration frequencies and sound velocities will be determined by m_h rather than by m_H, i.e., they will be larger by a factor $\sqrt{m_H/m_h} \sim 10$ (at $m_h \sim 20\, m_0$).

In hydrogen, the phase transition from the molecular crystal to the atomic crystal can be realized with the aid of a pressure of several megabars. In the excitonic phases, the role of the "pressure" is played by the width of the gap between the valence and conduction bands, which can give way to band overlap. In some substances the gaps can depend strongly on the external pressure or on the magnetic field. Thus, transitions between different excitonic phases are again ensured in final analysis by the external pressure. But the scale of these pressures in BiSb and CuCl is of the order of not more than several kbar, i.e., smaller by hundreds of times than in hydrogen.

Let us imagine qualitatively how the transitions occur with decreasing gap. When

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the gap reaches the value $(1/2)\mathrm{Ry}^* = m_e e^4/2\epsilon_0^2$, exciton production sets in. Of course, Van der Waals attraction forces act between the individual "atoms"–excitons–or "molecules"–biexcitons–and lead to a first-order transition into the condensed phase at a gap width somewhat larger than Ry*/2. We, however, will disregard this small effect. If the gap is less than Ry*/2, then the density of the excitons is determined by their repulsion at short distances. Consequently $n_e = n_h \sim (m_e e^2/\epsilon_0)^3$. In view of the exponential dependence of the repulsion forces on the distance, the density will change little with further decrease of the gap, until the band overlap becomes strong enough. Then a metallic phase sets in, which can be called "metallic excitonium." The condition for this is $e^2/\epsilon_0 v_e = e^2 m_e/\epsilon_0 p_0 \lesssim 1$, where p_0 is the limiting Fermi momentum determined from the condition $p_0 = \sqrt{2m_e(E_v - E_c)}$, where E_v and E_c are the edges of the bands (it is assumed that $E_v > E_c$, i.e., the bands overlap; the formula for p_0, strictly speaking, is valid only at $e^2/\epsilon_0 v_e \ll 1$). Obviously, for this purpose the band overlap must be $E_v - E_c \gtrsim \mathrm{Ry}^*/2$. If $m_h \gg m_e$, then it is still possible to have for holes $e^2/\epsilon_0 v_h \gg 1$, i.e., they can form a lattice.

Knowledge of m_e, m_h, and $E_v - E_c$ makes it possible in principle to obtain all the characteristics of the crystalline excitonic phases, but the numerical calculations are complicated. We confine ourselves therefore to some simple estimates for metallic excitonium in the limiting case $e^2\epsilon_0 v_e \ll 1$. The most interesting is the question of superconductivity. The most effective electron-interaction mechanism is exchange of exciton–lattice vibration quanta. In view of the Coulomb forces, it is easy to estimate the quantities that enter in the well known BCS-theory formula $T_c \sim \omega(2p_0)\exp(-1/\lambda)$. Namely, it turns out that $\omega(2p_0) \sim (p_0^2/m_e)(\sqrt{e^2 m_e/p_0\epsilon_0})\sqrt{m_e/m_h}$ and $\lambda \sim e^2 m_e/\epsilon_0 p_0$. In the metallic region $\lambda \lesssim 1$. With decreasing overlap, λ is increased both by the decrease of p_0 and by the increase of the effective mass of the electron m_e^* when the role of the interaction with the lattice increases (this tendency can be traced in the limiting case $\lambda \ll 1$, but it is preserved in all probability also at $\lambda \sim 1$). It is clear that although the increase of the band overlap contributes to the onset of the metallic excitonium, the critical temperature is decreased in this case. The maximum attainable critical temperature is obtained at $\lambda \sim 1$. In this case there is only one scale for the electron energies, namely Ry*, and thus

$$T_{c\,max} \sim \frac{m_e e^4}{\epsilon_0^2}\sqrt{\frac{m_e}{m_h}}.$$

If $m_e \sim 0.2m_0$, $\epsilon_0 \sim 1$–3, and $m_e/m_h \sim 0.01$, then this can amount to several hundred degrees.

Thus, we can count on obtaining a rather high critical temperature. As to the critical field, it will not be so strong as might be assumed on the basis of the proportionality of H_c and T_c. According to the BCS theory $H_c \sim T_c\sqrt{m_e p_0}$. This yields

$$H_c \sim \epsilon_0^{-1/2} p_0^2 e\sqrt{m_e/m_h}\exp(-1/\lambda),$$

at $\lambda \ll 1$ and $H_c \sim (e/r_B^*\epsilon_0^{1/2})\sqrt{m_e/m_h}$ at $\lambda \sim 1$ (r_B^* is the effective Bohr radius). Thus, the critical field increases with decreasing overlap. The maximum value of the field at

$m_0=0.2m_0$, $\epsilon_0\approx 2$, and $m_e/m_h\sim 0.01$ is of the order of 10^4 Oe. It is of interest to determine the behavior of κ. It is known that $\kappa=0.96\ \delta/\xi$ where $\delta=\sqrt{m_e c^2/4\pi n_e e^2}$, $\xi=0.18\ v/T_c$, and n_e is the electron density. This yields $\kappa\sim c/v\sqrt{m_e/m_h}\exp(-1/\lambda)$, i.e., κ decreases with increasing band overlap. As $\lambda\to 1$ we get approximately $\kappa\sim\epsilon_0/\alpha\sqrt{m_e/m_h}$, where α is the fine-structure constant ($\alpha=e^2/\hbar c=1/137$). If $m_e/m_h\sim 0.01$, then $\kappa\sim 10$, i.e., if the overlap is not too large even pure metallic excitonium is a type-II superconductor. The corresponding $H_{c2}\sim\kappa H_c\sim 10^5$ Oe.

The increase of m_e^* on account of the Coulomb interaction with the hole lattice contributes to an increase of the maximum values of T_c, H_c, and κ.

Let us see what bearing these arguments can have on CuCl. According to[4], at temperatures below 200–300K this substance has three phases, two dielectric (0–6 and 6–40 kbar) and one metallic (40–100 kbar). These are room-temperature pressures. The energy spectrum has according to[5,6] a valence-band maximum at the point Γ, with a mass $m_h\sim 20m_0$, and conduction-band minima at the points Γ and X. The width of the direct gap at the point Γ is $\Delta_{\Gamma\Gamma}=3.4$ eV, and the corresponding electron mass is $m_e=0.34m_0$. The width of the indirect gap is $\Delta_{\Gamma X}<0.35$ eV and the corresponding electron mass is more likely smaller than the mass of the first electronic minimum. There are data indicating that the indirect gap decreases with increasing pressure. Thus, the ratio of the electron and hole masses is $m_h/m_e\sim 100$, and the width of the gap (or the overlap) can be regulated by external pressure. It is clear that CuCl is a suitable candidate for searches for the described hypothetical situation.

According to[7,8], a smeared transition into the diamagnetic phase ($\chi=-\alpha/4\pi$, $\alpha\sim 1$) is actually observed in the 100 K region, and the transition temperature increases as the pressure is removed.[1)] This agrees qualitatively with the described regularities of T_c, although no superconductivity was observed directly in the experiment. An interesting feature of the metallic phase is also that it is preserved when the pressure is removed, down to ~ 1 kbar at 200 K. Diamagnetic states arise also in other phases,[1,9], but always only under conditions of rapid cooling or heating.

The following hypothesis can be advanced: The two dielectric phases observed at lower pressures are also condensed excitonic phases. What they really are cannot be ascertained without detailed experiments or calculations, but the possibilities are numerous: various crystalline modifications made up of rotating molecules or nonrotating molecules, an atomic antiferromagnetic dielectric, or finally an atomic or molecular exciton liquid. The energy differences between these phases are most likely small, as is evidenced by the small volume effects observed in the transitions. We note also that the transitions are most probably pure electronic, since the principal crystal lattice is isomorphic in all three phases. We can further assume that under nonequilibrium conditions a metallic phases can appear at low pressures and be preserved in a metastable state. This phase will be superconducting in an appropriate temperature region.

If this assumption is correct, then it follows that it is meaningless to study the details of the appearance of diamagnetic states under nonequilibrium conditions. On

the contrary metallic superconducting excitonium must be primarily investigated at high pressures, where it is an equilibrium phases, and attempts should then be made to preserve it as a metastable phase as the pressure is removed. It is possible that at a temperature in the 100 K range this phase can be brought down to zero pressure.

A distinguishing feature of CuCl are the very heavy holes. The reason is that the valence band stems mainly from the *d*-state of the copper atoms. It is natural to expect other substances of the same type to be found among the semiconducting or semimetallic compounds with valence bands made up of *d* or *f* atomic cation states.

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