

## Novel Superconductivity from an Insulator

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Superconductivity is one of the most remarkable phenomena in condensed matter physics. In spite of its simplified model Hamiltonian and the mean-field treatment, the theory of Bardeen, Cooper, and Schrieffer (BCS) is successful in explaining all the basic properties of usual superconductors. The core of the BCS theory is the Cooper instability. Namely the normal metallic state is unstable against an infinitesimal attractive interaction between electrons near the Fermi surface.

In recent years, however, novel types of superconductors are found near the insulating phases in the organic materials and the copper oxides. It seems that the phonon mediated BCS theory is not able to explain the high temperature transitions at least in the oxides. The obstacle against high  $T_c$  is to obtain a strong electron-phonon coupling  $\lambda$ . Furthermore even if one obtains a large  $\lambda$ , the renormalization effect ( $\lambda \rightarrow \lambda/(1 + \lambda)$ ) prevents high  $T_c$  as shown by the Eliashberg strong-coupling theory. A Fermi surface is responsible both for the reduction of the electron-phonon coupling due to the screening effect and for the renormalization of the coupling constant. These obstacles may be avoided in an insulator.

Insulators are also interesting in relation to the large diamagnetic anomalies observed at temperatures as high as 200 K in some specially prepared samples of CuCl under high pressures[1]. If we interpret the anomalies as the occurrence of superconductivity, we have a very unique situation in which a semiconducting phase showing an electronic resistivity with a finite activation energy enters directly into a superconducting phase through not a second- but a first-order phase transition at such a high temperature. A similar phenomenon has also

been observed in pressure-quenched (i.e., prepared by releasing high pressures at a rapid rate) samples of CdS at 77 K[2].

We investigate a possibility of a new superconducting instability which could take place even in an insulator in which no Fermi surface exists[3]. Our theory predicts a possibility of superconductivity brought about directly from a semiconducting phase through a first-order (or second-order) phase transition for the first time. Consider a system composed of a filled valence band and an empty conduction bands. The Fermi level  $\mu$  lies in the middle of the gap of the one-particle spectrum. Thus the system is an insulator. The fermion annihilation operators for the valence band and the conduction band are denoted by  $a_{k\sigma}$  and  $b_{k\sigma}$ , respectively. If the gap  $G$  is larger than the Debye cutoff energy  $\omega_c$ , the normal state is stable against the Cooper pairing  $\langle a_{k\uparrow}a_{-k\downarrow} \rangle$  because of the absence of states in phase space for multiple scatterings to form the pair. This is the case even if  $\lambda$  is very large. Note, however, that the same attractive potential works between a pair of electrons in different bands. When electrons in the valence band are partially promoted to the conduction band to make a pair  $\langle b_{-k\downarrow}a_{k\uparrow} \rangle$ , there is a plenty of room for the multiple scattering even for  $\omega_c < G$ . Thus we may have superconductivity originating from a new type of pairing  $\langle b_{-k\downarrow}a_{k\uparrow} \rangle$  rather than the usual Cooper one. This new pairing gives a gap equation which is quite different from the BCS theory. This leads to many unusual properties, although the superconducting state itself is found to be similar ( the Meissner effect, the infinite conductivity,  $2e$  flux quantization *etc.*).

The superconducting transition temperature  $T_c$  is of the order of the gap between the two bands. The universal relations in the BCS theory like  $\Delta(0)/T_c$ ,  $\Delta(T)/\Delta(0)$ ,  $H_c(T)/H_c(0)$ , and  $\Delta C/C_n$  do not hold in the present model. They depend on the coupling constant  $\lambda$ , the cutoff energy  $\omega_c$ , and the normal-state properties like the single particle energy. In some regions of  $\lambda$  and  $\omega_c$  it is possible to have a first-order superconducting transition. When  $T_c$  is not much larger than the gap energy  $G$ , there are only a few thermally excited carriers in the normal state near  $T_c$ . Therefore we have, for the first time, a unusual insulator(or

semiconductor)-superconductor first-order phase transition. This is consistent with the experimental situation in CuCl.

Since superconductivity takes place when  $U$  is of the order of  $G$  in our model, the theory should treat the strong correlation in a non-perturbative way and the band picture may not be appropriate. We have employed the mean-field treatment, but its validity must be examined. Note also that even the normal state provides a rather non-trivial problem. These questions can be addressed in one-dimensional systems in which the exact results by the Bethe ansatz method are available[4].

In applying the present theory to real solids, we need to include the effects of a weak non-symmetry in  $\epsilon_a(k)$  and  $\epsilon_b(k)$ . However, it can be shown that this does not lead to a drastic change in the predictions of the theory. Perhaps the most important question is the origin of a strong attractive interaction which gives  $\lambda \geq 2$ . One of the simplest candidates is the exchange of phonons as in the BCS theory. There is a possibility to have such a large  $\lambda$  from optical phonons in some insulators in which a strong electron-phonon interaction is not screened at all. We also need to know about the retardation effects of phonons. In addition, the reduction mechanism of the Coulomb repulsion[5] should be reconsidered in the present pairing model. Another candidate for an attractive interaction is an electronic origin, either charge fluctuations like excitons[6] or spin fluctuations. Whatever the origin of the attractive force is, we have to treat a completely new many-body problem for superconductivity, namely, an *instability without a Fermi surface*.

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