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Possibility of insulator to superconductor phase transition

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Résumé. — On propose qu'un système avec un fort couplage électrons-phonons est un isolant bipolaronique au-delà d'une constante de couplage critique. Ceci donne la possibilité d'une transition de phase d'un état supraconducteur à l'état isolant à $T = 0$ quand on varie la constante de couplage.

Abstract. — A phase diagram is postulated where the ground-state of a strongly coupled electron-phonon system is a bipolaronic insulator beyond a critical coupling strength. This opens up the possibility of phase transition from a superconductor to insulator at $T = 0$, as the coupling is varied.

It is generally believed that a superconductor is metallic in its normal state. We propose that the complete phase diagram must contain a branch where the superconducting state becomes insulating above the transition temperature T_c.

In a series of recent papers the existence of a bipolaronic ground-state in a great variety of non-metallic transition metal compounds has been both postulated [1] and demonstrated [2]. These bipolarons can be thought of as localized Cooper-pairs (a pair of up-spin down-spin electrons on near-neighbour sites) that are stable as long as the deformation-induced mutual attraction term $\frac{g_0^2}{M\omega_0^2}$ exceeds the mutual Coulomb repulsion v, where g_0 is an optical electron-phonon coupling constant, M is the atomic mass and ω_0 is an optical frequency. These bipolarons stand exactly in the same relationship to B.C.S. superconducting pairs as does a localized electron to an itinerant one.

The analogy between the two kinds of electron pairs is very close indeed and is the subject of a fuller paper [3] under preparation. In order to see this analogy simply, we may naturally ask the question as to what happens to a B.C.S. pair as we increase the electron-phonon coupling. The McMillan formulation [4] of the B.C.S. theory of superconductivity gives us, in the strong-coupling limit T_c as a function of λ, the dimensionless electron-phonon coupling constant which is given by

$$\lambda = \frac{N(0) \langle g^2 \rangle}{M \langle \omega^2 \rangle} \qquad (1)$$

where $N(0)$ is the density of electronic states of one spin at the Fermi level/eV-atom.

$\langle g^2 \rangle$ is the electron-phonon coupling constant averaged over the Fermi surface,

and $\langle \omega^2 \rangle$... some averaged acoustic phonon-frequency squared.

We may note that $\frac{g_0^2}{M\omega_0^2}$ is the maximum binding energy of a bipolaron, if the Coulomb repulsion term is ignored and a $\lambda_{\max}$ corresponding to some maximum electron-phonon coupling constant for bipolaron formation can be defined. Here both g_0 and ω_0 correspond to optical phonons, especially the $k = 0$ mode. As an example, a value of $\lambda_{\max}$ can be obtained for the bipolarons in Ti_4O_7 for which we have the most extensive data. Using a binding energy of bipolaron formation of 0.6 eV as equal to $\frac{g_0^2}{M\omega_0^2}$ with $N(0)$ equal to 5 states/eV-atom as obtained from the Pauli susceptibility measurements, we obtain a $\lambda_{\max} = 3.0$, which is much larger than that observed experimentally for all known superconducting materials. We can use the strong-coupling parameter λ to describe two limiting behaviours of the ground-state of a strongly coupled electron-phonon system.

(*a*) In the limit $\lambda < 1$, the McMillan expression for the superconducting transition temperature T_c reduces to the B.C.S. expression

$$T_c \sim \langle \omega \rangle \exp - \left| \frac{1 + \lambda}{\lambda} \right| . \qquad (2)$$

Although this means that even for an infinitesimally small λ, T_c will be non-zero, for all real practical purposes T_c is very small below a $\lambda \sim 0.1$ (e.g, Na would be superconducting with a $T_c \sim 10^{-3}$ K !) and we can use a critical value of λ, as a threshold for the appearance of superconductivity. For most metals and alloys that become superconducting, $\lambda \sim 0.1$ to 1 [4]. The full strong-coupling McMillan expression for T_c shows saturation of T_c beyond $\lambda \sim 2$ (the so-called $\lambda = 2$ limit for maximum temperature superconductivity). Allen and Dynes [6] have shown that this T_c maximum is an artifact of the McMillan expression, and in reality T_c should continue to increase with $T_c \sim \sqrt{\lambda}$ when λ is as large as 10 or beyond. We do not think that this has any physical meaning, and that, on the contrary, some sort of saturation and eventual decrease of T_c with λ must occur before that.

This merely underlines the necessity that in the McMillan-Allen-Dynes formulation the renormalization of the $\langle \omega^2 \rangle_{av}$ must be included in such a way that in the strong coupling limit $\langle \omega^2 \rangle_{av} \to 0$, as $\lambda \to \lambda_2$ leading to a $T_c \to 0$. The point $\lambda = \lambda_2$ is precisely where the local deformation is *static* rather than *virtual*.

(*b*) We know that in the large λ limit, bipolaron formation occurs. For a simple square density of states of bandwidth W and a half-filled band, the metallic state is unstable to bipolaron formation, if the binding energy E_b of bipolarons $\left(E_b = \dfrac{g_0^2}{M\omega_0^2}\right)$ exceeds $W/2$. This gives us a $\lambda_2 = 2.5$ as the second limit on the electron-phonon coupling constant at which the metallic state becomes insulating at $T = 0$. We can thus postulate that at a second critical electron-phonon coupling constant $\lambda = \lambda_2$, $\lambda_2 > \lambda_1$ the ground-state will be bipolaronic.

(*c*) At $T \neq 0$, the insulating ground-state of the bipolarons eventually transforms to a metallic state as has been shown by the extensive experimental work of C. Schlenker [7] and her group.

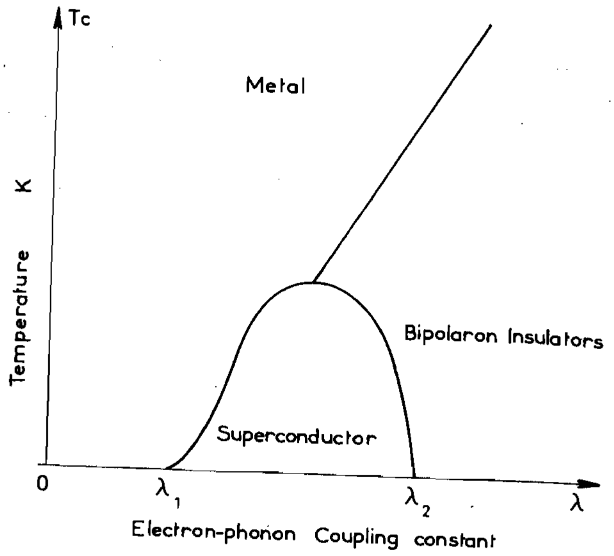

Fig. 1. — Phase diagram as a function of electron-phonon coupling strength.

From the considerations (*a*), (*b*) and (*c*), the composite phase-diagram as a function of the electron-phonon coupling parameter λ must look like figure 1. It is thus seen that a superconductor to insulator phase transition must inevitably occur.

Several points are to be noted. At $T = 0$, this transition, we believe, will occur abruptly and will be first order. The three phases cannot coexist at the point λ_2 at $T = 0$ because in the presence of any attractive pairing interaction between two electrons the eigen-states must be paired. The decrease of the superconducting temperature below a certain λ really reflects the instability of the lattice towards covalent bond formation (crystalline Be with a $T_c \sim 0.3$ K almost succeeds being a semiconductor like its neighbour B). This tendency of transition towards covalent non-metallic structure with increased λ was already pointed out by Anderson and Cohen [8].

Dr. Julius Ranninger of this laboratory raised as many objections to this paper as possible, but graciously conceded to me the phase diagram.

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