Effect of charging energy on superconductivity in granular metal films

B. Abeles
RCA Laboratories, Princeton, New Jersey 08540
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Previous model calculations of the superconducting properties of aggregates of superconducting grains coupled by Josephson tunnel barriers did not take into account the charging energy associated with small metal grains. It is pointed out that in granular superconductors, in which the grain size is 20–100 Å, the charging energy can be orders of magnitude larger than the Josephson coupling energy and superconducting coupling between the grains is quenched unless the grains are in intimate electrical contact.

During the past decade there have appeared in the literature several model calculations of the superconducting properties of aggregates of superconducting grains coupled by Josephson tunnel barriers.[1-6] The motivation for the work was to explain some of the unusual properties of granular superconductors.[7] Deutcher *et al.*,[6] on the basis of this model, derived critical temperature shifts and crossover regions between zero-dimensional and three-dimensional behavior of the aggregates, as a function of the tunneling coupling strength between the grains. It is the purpose of this note to point out that in the above theoretical treatments, no account was taken of the charging energy associated with small metal grains. The charging energy results from the fact that every metal grain has a small capacitance so that a finite energy is required to transfer an electron between grains. The existence of this charging energy has a profound effect on the superconducting coupling between grains. This result follows from the fact that in order for the coupling between two grains to be superconducting, the phase difference of the superconducting wave functions on the two grains, in the absence of a net current, must vanish. Because the phase and the number of electrons on a grain are conjugate variables,[8] setting the phase difference between two grains equal to zero, leads to an indeterminate number of electrons in each individual grain. This indeterminacy in the number of electrons results in charging of the grains. It is shown that unless the grains are in intimate electrical contact, the charging energy is much larger than the Josephson coupling energy. When this condition is met it follows, on the basis of a simple argument due to Anderson[8] that superconducting coupling between the grains is quenched.

Anderson[8] pointed out that the electrostatic energy associated with the capacitance of a Josephson junction results in zero-point oscillations of energy $\hbar\omega$, where

$$(\hbar\omega)^2=(e^2/C_j)E_j\ , \tag{1}$$

C_j is the junction capacitance, and E_j is the Josephson coupling energy. In order for the zero-point oscillations not to quench the Josephson coupling, the condition $\hbar\omega \ll E_j$ must be satisfied, or

$$e^2/C_j \ll E_j\,. \tag{2}$$

In a conventional Josephson tunnel junction, which was the case examined by Anderson, the junction area and consequently the capacitance C_j are large and the condition given by Eq. (2) is always satisfied. However in granular metal systems in which the grains are small (diameter ~20–100 Å), the junction capacitance formed by neighboring grains is very small and as we show below, e^2/C_j is considerably larger than E_j.

In the previous treatments of granular superconductors the model used[3,6] consisted of a simple cubic array of metal spheres of diameter d with nearest-neighbor distance $s+d$. The metal spheres were embedded in an insulating matrix and conduction was assumed to be due to tunneling through tunnel barriers of thickness s. The Josephson coupling energy E_j between neighboring grains is given by[9]

$$E_j=\hbar\Delta_0/8e^2R_j\,, \tag{3}$$

where R_j is the junction resistance, Δ_0 is the energy gap parameter at $T=0$, e is the electron charge, and $\hbar$ is Planck's constant. The junction resistance R_j was expressed in terms of the normal resistivity of the system ρ_n by the relation

$$R_j=\rho_n/(s+d)\,, \tag{4}$$

where it was assumed that all the junction resistances are the same. The energy required to transfer an electron from a neutral grain to a neighboring neutral grain, E_c^1 ($\equiv e^2/2C_j$), is given to a good approximation by[10]

$$E_c^1\simeq(e^2/\epsilon d)\,[s/(s+\tfrac{1}{2}d)]\ , \tag{5}$$

where ϵ is the dielectric constant of the insulator.

We use Eqs. (3)–(5) to calculate E_j and E_c^1 for the case of granular aluminum—a system which has been studied extensively.[2,3,7,11-14] It consists of a mixture of finely divided crystalline aluminum and amorphous SiO_2 or Al_2O_3. Typical values of the parameters for granular aluminum are[7,14] $\rho_n = 10^{-3}\ \Omega\,\text{cm}$, transition temperature $T_c = 2$ K, $\Delta_0 = 3\times 10^{-4}$ eV, $d = 30$ Å, $s = 5$ Å, and $\epsilon = 8.5$. Using the above numerical values in Eqs. (3)–(5), we compute $E_j = 5.4\times 10^{-5}$ eV and $E_c^1 = 0.015$ eV. Thus, the electrostatic energy e^2/C_j is 2–3 orders of magnitude larger than the Josephson coupling energy E_j and the junction, according to Eq. (2), is quenched. It should be noted that this result is independent of the type of coupling between the grains, i.e., R_j can be a tunneling resistance or a weak link such as a pinhole in the insulator.[15]

From the above considerations we conclude that in order for the coupling between grains to be superconducting, it is required that R_j be much lower than the value given by Eq. (4). Such low values of R_j, together with high values of ρ_n, can occur only in an inhomogeneous structure in which superconductivity is due to channels formed by grains in intimate electrical contact. These superconducting channels intersect at junction points which form a three-dimensional lattice. As long as the coherence length is much larger than the separation between junction points, the film is three dimensional. Breakdown of three-dimensional behavior occurs when the distance between junction points is larger than the coherence length, and T_c (as determined by a resistive transition) vanishes when there are no continuous superconducting channels. It should be noted that in the model of Deutcher *et al.*,[6] the criterion for three-dimensional behavior is given by comparing E_j with the superconducting condensation energy of a grain. The value of E_j according to this criterion is much lower than that required by Eq. (2).

Direct experimental evidence for the percolation structure of granular metals comes from electron microscopy studies.[7,10] These show that, in the compositional region where granular superconductors exhibit a nonvanishing T_c, the microstructure consists of a wide distribution of grain sizes in which there are grains surrounded by insulator and chains of touching grains. Evidence that charging energy and percolation effects play an important role in granular superconductors, comes from the fact that superconductivity (as determined by the resistive transition) vanishes in the compositional region (~0.5 vol fraction metal) where the temperature coefficient of resistivity changes from positive to negative,[3,7,12-14] and the conduction mechanism changes from percolation along chains of touching grains to thermally activated tunneling between isolated grains.[7,16] Evidence for imhomogeneous structure of granular superconductors was also found by Hauser[13] and Morozov *et al.*[17] from critical-field measurements. In conclusion we note that there may be other granular systems[5,18] in which the grains are sufficiently large for the charging energy to be low enough so that the condition $e^2/C_j \simeq E_j$ is satisfied. In such systems it would be interesting to search for the zero-point oscillations predicted by Eq. (1).

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