Hypothesis concerning the possible effect of nonequilibrium high-temperature superconductivity

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We describe a hypothesis concerning a possible effect of nonequilibrium high-temperature superconductivity. Studies of solutions of Na in ammonia, of (*TTF*), (*TCNQ*), and of chalcopyrite $CuFeS_2$ are discussed.

According to the modern BCS-Bogolyubov theory of *superconductivity*, a *strong electron-phonon interaction* must exist in a superconductor if it is to have a high superconducting transition temperature T_c. A strong electron-phonon interaction, however, leads to instability of the cyrstal lattice. This imposes a natural limit on the maximum attainable critical temperature, namely $T_c^{max} \sim \Theta_D/10 \sim 20-40\,^\circ K$. [1,2]

This raises the natural question whether high-temperature superconductors can be realized in essentially *nonequilibrium situations*, with an *electron-phonon* interaction that is large in principle and is produced in the metal during the course of its crystal lattice. [1)]

The aforementioned limitation imposed by the equilibrium theory on T_c^{max} can then be greatly lowered (although T_c can still not exceed apparently, the Debye temperature Θ_D or $\Theta_D/2$, if we stay within the framework of the usual electron-phonon superconductivity mechanism, the only one discussed in the present article).

The presence of a large electron-phonon interaction in a metal whose lattice is being realigned seems obvious to us since, first, the conduction electrons make the decisive contribution to the total cohesion energy of the metal and, second, in a metal whose lattice is being realigned it is utterly impossible to subdivide (even approximately) the overall complicated electron-nuclear quantum-mechanical system (such as a real metal is) into an electron subsystem and a phonon subsystem that is weakly coupled to it. Neither the adiabatic Born-Oppenheimer approximation nor the harmonic-oscillator approximation is suitable, and consequently the electron phonon interaction, which had been introduced into the theory exclusively to designate the total-Hamiltonian terms that violate these approximations, should formally be very large.

The optimal conditions for the observation of the effect of the nonequilibrium high-temperature superconductivity are such that the lattice realignment takes place simultaneously over the entire volume of the sample, but at the same time slowly enough to permit the superconducting state to form and to be able to register the onset of the superconductivity.

In perfect crystals, the lattice realignment in a phase transition occurs within a very short time. To register the superconductivity in this case it is necessary therefore to have special apparatus. In the case of poor cyrstals and polycrystalline samples in which the phase transition is greatly smeared out in temperature (i.e., it occurs at each fixed temperature in a small volume of the crystal), there can be no clearly pronounced effect.

A characteristic feature of nonequilibrium superconductivity is its dependence on the time: it exists only during the course of lattice realignment, so that at any fixed temperature the resistivity of the sample should increase continuously with time to the normal value as soon as the realignment process terminates.

The considerations advanced above apparently explain the onset of anomalous high conductivity in solutions of Na in ammonia. [3,4] The effect is observed only following a rapid cooling of the solution, when the sample goes rapidly (in nonequilibrium fashion) through the phase transition temperature, and there is no time for the structure realignment to be completed. The temperature to which the sample is cooled should be high enough for a structure realignment corresponding to an incomplete phase transition to be possible at this temperature (as a result of thermal activation). The rate of increase and the change of the resistivity should decrease when the samples are cooled to lower temperatures. In the case of abrupt cooling to liquid-hydrogen temperature and below, the structure of the solutions "freezes" and there should be no effect of nonequilibrium superconductivity[2)], while the electric resistance of the samples should be close to the equilibrium value for the metallic phase of the solutions at these temperatures, and much higher than the minimal registered resistivity at the temperature close to 77 °K.

It is quite possible that the poor reproducibility of the results in investigations of (*TTF*), (*TCNQ*), and their dependence on the measurement conditions, [5,6] and also the observed sharp increase of the electric conductivity of the $CuFeS_2$ films, [7] is due to superconducting fluctuations near the region of existence of nonequilibrium superconductivity.

One can expect nonequilibrium superconductivity to set in also in organic or metallo-organic compounds in low-temperature solid-phase chemical reactions, if they are accompanied by the appearance of a sufficiently large number of free electrons. Another interesting possibility of the appearance of nonequilibrium superconductivity may be the recrystallization of amorphous metallic films when the temperature is raised.

Of very great interest is the possibility of "stabilizing" nonequilibrium superconductivity by modulating the temperature in the phase-transition region. If the amplitude and frequency of the modulation are correctly chosen (for each concrete case), one can hope to observe nonequilibrium superconductivity during a prolonged time.

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[1)]We can, of course, imagine hypothetical substances that can undergo a polymorphic phase transition and simultaneously become superconducting in the vicinity of this transition. This can be accompanied by formation of a metastable unstable superconducting phase in some small vicinity of the temperature T_p of the polymorphic transition, if at the same time T_p is lower than a certain characteristic Debye temperature Θ_D, of the material, which characterizes the average speed of sound in both polymorphic modifications.

[2)]The effect of nonequilibrium superconductivity was apparently observed in[4] only in individual cases, in view of its extremely short lifetimes.

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