# Superconductivity and localization of electrons in disordered two-dimensional metal systems

### B.I. Belevtsev

Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, Kharkov Usp. Fiz. Nauk 160, 65–98 (January 1990)

A review is given of experimental and theoretical studies of changes in the superconducting properties of disordered two-dimensional metal systems as the metal-insulator transition is approached. Particular attention is devoted to ultrathin (including discontinuous and island) and granular films. The influence of disorder on the critical point  $T_c$ , the fluctuation conductivity above  $T_c$ , and the magnitude and temperature dependence of the upper critical field  $H_{c2}$  are discussed. The effects of film inhomogeneity and the associated percolation effects on superconductivity are examined in some detail. Mechanisms responsible for quasireentrant phenomena associated with the establishment of phase coherence of electrons in inhomogeneous systems are extensively discussed.

# I. INTRODUCTION

It is well known that an increase in the disorder of the crystal lattice of a metal tends to restrict the free motion of electrons. Modern ideas<sup>1-6</sup> suggest that a high enough degree of disorder gives rise to the complete localization of electrons in a bounded region of space (Anderson transition). In superconducting metals, an increase in disorder is accompanied by a reduction or, in the limit, complete suppression of superconductivity. There is considerable current interest in the change in the superconducting properties with increasing disorder and, in particular, the effects associated with the direct competition between localization and superconductivity. This has been dictated by practical needs such as the development of materials (their properties are almost always far from ideal) and by the fundamental importance of these studies, which each year have revealed new aspects of the quantum properties of electrons in metals. Thin twodimensional films in which localization effects are more clearly defined that in three-dimensional systems are widely used for these purposes.

In the Ginzburg-Landau theory (GL), the complex order parameter can be written in the form:  $\psi = \Delta \exp(-i\varphi)$ , where  $\Delta$  is the amplitude and  $\varphi$  the phase of this parameter. Hence, it follows that disorder can destroy superconductivity either by reducing the amplitude of the order parameter or by destroying the phase coherence of the superconductivity electrons. It has become clear in recent years that the relative contribution of each of these mechanisms depends on the degree of inhomogeneity of the superconducting object. The latter can be judged by considering the two characteristic lengths  $\xi_d$  and  $\xi_{CL}(T)$ , the first of which corresponds to the characteristic scale of inhomogeneity associated with disorder and the second is the GL coherence length. When  $\xi_d \ll \xi_{CL}(T)$ , the system behaves as a homogeneous one, and disorder affects largely the order parameter although the effects of disorder on the phase coherence of electrons cannot be totally excluded. On the other hand, when  $\xi_d \gtrsim \xi_{GL}(T)$ , the system is inhomogeneous. Examples of such systems are the granular or island films with topological disorder for which percolation effects are significant. The length  $\xi_{i}$  can then be the size of the granules or islands, or the characteristic percolation length  $\xi_{\rm p}$ . For inhomogeneous systems, the reduction in the critical temperature  $T_c$  that

accompanies increased disorder is largely due to the suppression of phase coherence between weakly coupled superconducting regions. Both mechanisms frequently operate at the same time in real objects.

In this review, published data are used as a basis for a discussion of proposed and experimentally verified mechanisms for the effect of disorder on the superconductivity of homogeneous and inhomogeneous two-dimensional films. Many of these mechanisms are also valid for three-dimensional systems, but their detailed properties are outside the scope of this review. Despite the considerable recent advances in our understanding of the electronic properties of disordered conductors,<sup>1-6</sup> the connection between localization and superconductivity is still not entirely clear. These questions are attracting considerable attention, and many publications appear in this field each year. The references listed at the end of this review do not claim to be complete, but will, we hope, represent the more important areas of research in this field in recent years. We shall confine our attention to films of standard superconducting materials. Nevertheless, a considerable proportion of the fundamental results that have now been established concerning the mutual influence and competition between localization and superconductivity (especially in inhomogeneous systems) is also valid for high- $T_c$  superconducting ceramics.

Our review is arranged as follows. Sec. 2 examines the change in the electronic properties of metal systems as the metal-insulator transition (MIT) is approached. This subject has been adequately reviewed in the literature, <sup>1-6</sup> and we shall therefore confine our attention to two-dimensional systems and to questions that have a direct bearing on the connection between localization and superconductivity. In Sec. 3, we examine the effect of greater disorder on superconducting properties such as  $T_c$ , the upper critical field  $H_{c2}$ , and the fluctuation superconductivity above  $T_c$ . In Sec. 4, we examine the effects of direct competition between localization and superconductivity as manifested, above all, in quasireentrant effects. In the final section (Sec. 5), we summarize the current state of this problem, and briefly examine some unresolved problems.

The effect of disorder on superconductivity is considered separately for homogeneous and inhomogeneous films. By homogeneous films, we mean continuous single-phase films of metals or alloys. There is a much greater variety of inhomogeneous objects. Our discussion will focus on granular and island films and disordered mixtures of a metal and a dielectric. Although the conductivity of these systems is largely determined by percolation effects, their behavior is significantly different in many cases, and must therefore also be considered separately. The behavior of homogeneous and inhomogeneous films will be compared in the course of oupresentation.

#### 2. VARIATION IN THE ELECTRONIC AND SUPERCONDUCTING PROPERTIES OF METALLIC SYSTEMS DURING THE METAL-INSULATOR TRANSITION

For homogeneous objects, the degree of disorder is described by the quantity  $\lambda \approx (k_F l)^{-1}$  where  $k_F$  is the Fermi wave number and l is the elastic scattering length of electrons. When  $\lambda \ll 1$ , the effect of disorder is small but, in the limit of great disorder,  $(\lambda \sim 1)$ , all the electron states must be localized. For two-dimensional systems, we have

$$\lambda = \frac{e^2 R_{\Box}}{2\pi^2 \hbar} \tag{2.1}$$

where  $R_{\Box}$  is the resistance of a square sample and e is the charge of an electron. A generally accepted theory of MIT is not yet available, although each of the existing theoretical approaches produces a reasonable description of a range of disordered systems.<sup>1-6,8</sup> For systems lying on the metal side of the MIT, the scaling theory is the main approximation.<sup>3,5,6</sup> According to this theory, all the electron states of two-dimensional systems must be localized (at least for T=0) whatever the degree of disorder. However, experimental data9,10 suggest that, at finite temperatures, the transition to strong localization occurs only for  $R_{\Box} \gtrsim 20-30 \text{ k}\Omega$ . Nevertheless, for a low degree of disorder ( $\lambda \ll 1$ ) and low enough temperature, we already observe appreciable deviations in the behavior of conductivity from the free-electron model, which give rise to quantum corrections to conductivity [weak localization effects (WLE) and electron-electron interaction (EEI)]<sup>3-5</sup>

The scaling theory of localization was developed without taking into account EEI effects. We shall not go into the different models whereby these effects can be taken into account in MIT (Refs. 2, 4, 6, 8, 11, and 12) and will merely note that, even when the degree of disorder is small, there should be deviations in the behavior of the electrons from the Fermi fluid theory.<sup>4</sup> This leads to a singularity in the density of states of electrons at the Fermi level  $N(F_{F'})$  (Ref. 4). In addition, the character of EEI itself is found to change.<sup>4,5</sup> All this must influence superconducting properties as well. Under the conditions of strong localization, the Efros-Shklovskiĭ theory<sup>2</sup> shows that the inclusion of long-range Coulomb repulsion leads to the appearance of the Coulomb gap. One of the possible reasons for the suppression of superconductivity as we approach the MIT may therefore be the depression of  $N(E_F)$ . On the other hand, Mott has shown<sup>1</sup> that  $N(E_F)$  can remain finite across the Anderson transition because it is only the position of the Fermi energy  $E_F$  relative to the mobility threshold  $E_c$  that is of primary importance. The correlation between  $N(E_F)$  and  $T_c$  was examined in Ref. 13 for granular aluminum films. Tunneling measurements were used to confirm the presence of corrections to  $N(E_F)$  due to EEI effects.<sup>4</sup> The reduction in  $T_c$  with increasing disorder was found to correspond to a reduction in

 $N(E_F)$ . Apart from  $N(E_F)$ , an increase in disorder can also affect the other characteristics of a system of interacting electrons and phonons in metals, e.g., the electron-phonon interaction (EPI), EEI the rate of inelastic and phase relaxation, and so on. The effects of disorder on superconductivity that are associated with these and other factors will be examined in detail below. For the moment, let us consider the principal experimental facts. In homogeneous metal systems, a high degree of disorder may be due to the presence of impurities and lattice defects, and this gives rise to a short mean free path length l. The effect of an increase in the number of lattice defects on  $T_c$  was first noted for films of simple metals deposited on a liquid-helium cooled substrate.<sup>14-16</sup> These and subsequent studies of cold-deposited films (see the reviews in Refs. 17-19) showed that an increase in disorder in weak superconductors such as Al, In, and Sn, produced an increase in  $T_c$ , whereas, in classically strong superconductors such as Pb, Hg, and amorphous Bi, the result was a reduction in  $T_c$ . It was shown later that strong enough disorder eventually always led to a reduction in  $T_c$ . The result of this for metals such as aluminum<sup>20</sup> or indium<sup>21,22</sup> is that the graph of  $T_c$  as a function of  $R_{\Box}$ , or of the resistivity  $\rho$ , acquires a maximum (Fig. 1). For indium films with a monotonic dependence of  $T_c$  on disorder, it was found that there were the following correlations between changes in  $T_{\rm c}$ and conductivity. In the region in which  $T_c$  increases with increasing  $R_{\Box}$ , indium films exhibit the normal temperature dependence of resistance, typical for metals. The reduction in  $T_c$  with increasing  $R_{\Box}$  begins for  $R_{\Box} \gtrsim 0.5$  k $\Omega$ . The films then have a small negative temperature coefficient of resistance that corresponds to the effects of weak localization and the electron-electron interaction.<sup>35</sup> This behavior is probably a reflection of weak localization and EEI on  $T_c$ , and will be examined below.

Interesting data on homogeneous lead films were obtained in Ref. 23 as a result of tunneling measurements. It was found that the ratio  $2\Delta/kT_c$  remained practically constant as the degree of order increased (Fig. 2). Another significant result reported in Ref. 23 is the discovery of a discrepancy between the phonon structure of tunneling spectra and the usual Eliashberg formalism for sufficiently high degree of disorder. A change in the Coulomb interaction due to disorder is suggested as a possible cause of such behavior.

In inhomogeneous systems, the MIT is determined by the combined influence of localization and percolation ef-



FIG. 1. Dependence of  $T_c$  on the resistivity at T = 4.2 K for granulated Al films.<sup>20</sup>



FIG. 2. Dependence of  $T_c$  (a) and  $2\Delta/kT_c$  (b) on  $R_{\Box}$  for inhomogeneous Pb films.<sup>23</sup> Numbers shown against the top axis indicate typical film thickness in Ångstroms.

fects. This also influences superconducting properties. For example, one of the indicators of the effect of inhomogeneity is the expansion of the size of the thermal region of the superconducting transition. It has also been noted that inhomogeneous systems exhibit a much weaker reduction in  $T_c$  with increasing  $\rho$  or  $R_{\Box}$  (Fig. 3). When percolation effects predominate,  $T_c$  is practically independent of  $\rho$ , and conductivity and superconductivity vanish simultaneously at the percolation threshold (cf. the behavior of the Pb-Ge system in Fig. 3).

Significant data on changes in superconducting properties of inhomogeneous systems approaching the MIT have been obtained as a result of tunneling experiments.<sup>25,26</sup> For granulated and almost island films of Al, Sn, and Pb, it was found that the superconducting gap  $\Delta$  spread out with increasing disorder (Fig. 4). The tunneling density of states was found to be N( $E,\Gamma$ ) = Re[ $E/(E^2 - \Delta^2)^{1/2}$ ], where  $\Gamma$ is the gap diffuseness parameter which increases with in-



FIG. 3. The function  $T_c(\rho)$  for systems with a high degree of inhomogeneity<sup>24</sup> ( $T_{c0}$  and  $\rho_0$  correspond to pure metals)  $\rho_0 = 1.8 \times 10^{-5} \Omega$  cm (Hg-Xe) and  $2.2 \times 10^{-4} \Omega$  cm (Bi-Kr). The most homogeneous is the Bi-Kr system and the least homogeneous the Pb-Ge system.



FIG. 4. Density of states N(E) for granulated Al films with normal resistivity of  $8 \times 10^{-3}$  (a) and  $\approx 2 \times 10^{-2}$  (b)  $\Omega$  cm (Ref. 25). Solid lines density of states deduced from tunnel data, dashed lines—density of states calculated from the BCS model with allowance for the spreading of the superconducting gap under the influence of disorder.  $\Gamma$ -gap spreading parameter.

creasing disorder (Fig. 5), so that superconductivity becomes gapless (Fig. 4). It was proposed in Ref. 26 that  $\Gamma$  was determined by the inelastic relaxation of electrons, the importance of which increases with increasing disorder. This is supported by the correlation found in Ref. 26, namely,  $2\Gamma \approx \hbar/\tau_i$ , where  $\tau_i$  is the inelastic relaxation time.

There is experimental evidence  $^{10,27,28}$  for the fact that the MIT in granulated films, which occurs as the thickness



FIG. 5. Twice the gap spreading parameter  $2\Gamma$  (due to the inelastic scattering of electrons) as a function of the resistance  $R_{\Box}$  for Sn films ( $\Delta = 0.74$  meV; Ref. 26).

of the dielectric interlayers between granules increases, is accompanied by the appearance of a Coulomb gap in the density of states, in accordance with the theory given in Ref. 2. However, it has been shown<sup>10,22</sup> for granulated indium films that the Coulomb gap of these inhomogeneous systems affects mostly the hopping conductivity of single-particle excitations. The superconducting properties of such objects are determined mostly by processes leading to the establishment of phase coherence between adjacent granules by means of Josephson coupling.

The following interesting property of two-dimensional ultrathin superconducting films was discovered in recent years. It has been found that there is a threshold resistance  $R_c = aR_Q$  above which phase coherence does not involve the entire sample<sup>29-31</sup> (*a* is a constant of the order of unity and  $R_o = \pi \hbar/2e^2 \approx 6.45 \text{ k}\Omega$  is the quantum of resistance). When  $R_{\Box} \gtrsim R_c$ , the resistance does not vanish as the temperature is reduced. The figure  $R \approx 6 \,\mathrm{k}\Omega$  is relatively universal and is independent, for example, of the thickness and material of the film (Figs. 6 and 7). As  $R_{\Box}$  increases toward  $R_c$ , ultrathin films are no longer continuous although they still do not consist of separate isolated islands. The superconducting properties of such films are determined by the processes responsible for the establishment of phase coherence between weakly coupled superconducting regions. The theoretical description of such systems is usually based on different models of coupled Josephson contacts, taking into account the effect of dissipative processes on quantum fluctuations of phase. Dissipative processes (due to the presence of the normal components of current in the contacts) may be associated with quasiparticle tunneling or normal shunting bridges in the contacts. The so-called resistive model of the Josephson junction is often used in this context (Refs. 32-33). Either way of taking into account dissipative processes can explain the existence of the threshold resistance  $R_c \approx 6$ k $\Omega$  (Refs. 34-39) although the normal ohmic bridges between weakly coupled superconducting regions should play the dominant part in ultrathin discontinuous films. Quantum phase fluctuations in dissipative systems can also be the reason for quasireentrant phenomena.<sup>40,41</sup> This will be discussed in Sec. 4.



FIG. 6. Dependence of  $R_{\odot}$  at 14 K on the thickness of Sn and Ga films.<sup>31</sup> Each pair of points corresponds to a given film. Open symbols—resistance does not fall to zero with decreasing temperature (there is no global superconductivity), full symbols—the resistance falls to zero after the mean thickness has been increased by a fraction of an Ångstrom. Dashed line represents  $R_{O} = \pi \hbar/2e^{2}$ .



FIG. 7. Resistance of Ga and Pb films at 0.7 K as a function of resistance in the normal state at 14 K (Ref. 30).

We note in conclusion that there has been some recent controversy about whether superconductivity vanishes during the transition to the dielectric state [the so-called superconductor-insulator transition (SIT)] or whether superconductivity is totally suppressed first and the metal-insulator transition follows [this is the so-called superconductor-metal-insulator transition follows [this is the so-called superconductor-metal-insulator transition (SMIT)]. The theoretical possibility of SMIT relies either on enhanced spin fluctuations with increasing disorder under the conditions of strong Coulomb interaction<sup>42</sup> (for three- and two-dimensional systems) or on the effect of the spin-orbit interaction<sup>43</sup> (exclusively for three-dimensional systems). Experiments with inhomogeneous systems<sup>44-46</sup> have not confirmed unambiguously the possibility of SMIT, and the problem requires further investigation.

# 3. EFFECT OF INCREASING DISORDER ON SUPERCONDUCTING PROPERTIES

# 3.1.Critical temperature $T_c$

#### 3.1.1. Homogeneous systems

3.1.1-1. Weak disorder. According to the classical theory of superconductivity,<sup>47,48</sup> weak disorder associated with nonmonotonic impurities has no effect on  $T_c$  (Anderson theorem). Strong enough disorder can, however, affect any characteristic of a system of interacting electrons and phonons in metals, and hence give rise to a change in  $T_c$ . In the Bardeen-Cooper-Schrieffer (BCS) model, the critical point is given by

$$T_{\rm c} = 1.14\omega_{\rm D} \exp\left(-\frac{1}{\lambda_{\rm ep}-\mu^*}\right), \qquad (3.1)$$

where  $\omega_{\rm D}$  is the Debye frequency,  $\lambda_{\rm ep}$  is the EPI constant  $\mu^*$  is the Coulomb pseudopotential, and

$$\lambda_{\rm ep} = 2 \int g(\omega) \, \omega^{-1} \mathrm{d}\omega, \qquad (3.2)$$

where  $g(\omega)$  is the Eliashberg function that depends on the density of phonon states and EPI.

For superconductors with strong EPI, it is common to use the McMillan formula<sup>49</sup>

$$T_{\rm c} = \frac{\omega_{\rm D}}{1.45} \exp\left[-\frac{1.04 \left(1 + \lambda_{\rm ep}\right)}{\lambda_{\rm ep} - \mu^* \left(1 + 0.62 \lambda_{\rm ep} \mu^*\right)}\right].$$
 (3.3)

It follows from (3.1) and (3.3) that the changes in  $T_c$  produced by a change in disorder can be due to the corresponding changes in  $N(E_F)$ , EPI, and effective EEI. The possible changes in these characteristics are usually taken into account in the first instance when the effect of disorder on  $T_c$  is examined. As an example, let us consider the suggested reasons for the increase in  $T_c$  in cold-deposited films of metals with weak EPI (Al, In, Sn).<sup>17,18</sup> Tunneling experiments have shown that, as disorder increases ( $\rho$  or  $R_{\Box}$  increases), there is a change in the function  $g(\omega)$  whereby the values of  $g(\omega)$  become greater for low  $\omega$ . This may be due to stronger EPI in disordered systems.<sup>17,18,50</sup> According to (3.2), this type of change in  $g(\omega)$  leads to greater  $\lambda_{ep}$  and, correspondingly, greater  $T_c$  (this does not take into account the possible effects of disorder on  $N(E_F)$  and  $\mu^*$ . The above considerations are not valid for superconductors with strong EPI, such as lead, for which greater disorder and amorphization lead to analogous changes in  $g(\omega)$  (Ref. 51), but T<sub>c</sub> decreases<sup>15,52</sup> instead of increasing.<sup>1)</sup> This difference in the behavior of weak and strong superconductors has long been known, and a possible explanation of it is given in Ref. 53, in which account is taken of the competition between attractive and repulsive effective EPI. This is one of a number of examples showing that, at present, we still do not have sufficiently universal mechanisms for the effect of disorder on  $T_c$  that could be used for a wide range of superconductors. This has probably been responsible for the emergence of a variety of models of the effect of disorder on superconductivity, each with its own limited range of validity.

There is no doubt that strong enough disorder will always reduce  $T_c$ . For films of the classical strong superconductors, for example, amorphous bismuth and gallium,<sup>54</sup> it has been found that  $T_c$  and  $R_{\Box}$  are correlated as follows:

$$\delta = \frac{T_{co} - T_c}{T_{co}} = qR_{-} \tag{3.4}$$

where  $T_{c0}$  is the unperturbed value of  $T_c$  and  $q \approx 10^{-4} \Omega^{-1}$ . This empirical relationship is valid for  $\delta \leq 1$ , for weak disorder. One of the first explanations of (3.4) in the case of twodimensional films was based on fluctuations in the electromagnetic field and in the order parameter.<sup>55</sup> The influence of disorder and of Coulomb effects on  $T_c$  was examined in Ref. 56 in the BCS approximation. A similar approach, but including weak localization and EEI was used in Ref. 57 to show that

$$\ln \frac{T_{\rm c0}}{T_{\rm c}} = g\lambda \left(\frac{1}{2}b^2 + \frac{1}{3}b^3\right), \qquad (3.5)$$

where g is the dimensionless EEI constant of the order of unity,  $b = |\ln(\hbar/kT_c\tau, \tau)$  is the elastic relaxation time, and  $\lambda$ is given by (2.1). The first term in (3.5) is the correction to the density of states, and the second represents the effective pairing EEI. When  $\lambda \leq 1$ , (3.5) is approximately the same as (3.4). A generalization of the theory of Ref. 57 to the case of stronger disorder is given in Ref. 58. The theory of Ref. 57 agrees with experimental data on Mo-Ge films<sup>59</sup> for  $R_{\Box} \leq 0.5$  (Fig. 8) when g = 0.6. Better agreement with these experimental data was achieved in Ref. 58. The theories presented in Refs. 57 and 58 are valid for weak localization with  $\tau^{-1} < \omega_D$ , but are probably invalid for  $R_{\Box} \gtrsim 1$  (the extension of the theory to the case  $\tau^{-1} > \omega_D$  is given in Ref. 60).

Experimental data thus show that even weak disorder  $\lambda \leq 1$  will affect EEI and EPI processes and, hence, the mag-

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FIG. 8.  $T_{\rm c0}/T_{\rm c0} = f(R_{\odot})$  for different compositions of amorphous Mo-Ge films.<sup>55</sup> The solid lines correspond to the theory of Ref. 57.

nitude of  $T_c$ . Existing theoretical models enable us to understand the overall character of these effects. The most successful is the explanation of the reduction in  $T_c$  under the influence of weak disorder when weak localization and EEI effects are taken into account.

3.1.1-2. Strong disorder. The suppression of superconductivity in homogeneous systems in the case of strong disorder  $\lambda \leq 1$  has been investigated experimentally but only to a very limited extent (Sec. 2). In particular, we know very little about correlations between changes in  $T_c$  and other characteristics of the superconducting state at the MIT threshold, on the one hand, and the corresponding changes in the different properties of interacting electrons and phonons in conducting systems, on the other. However, a major theoretical effort has been made in this area to separate, and often experimentally to justify, different ideas on the suppression of superconductivity in the case of strong disorder. Many of these ideas refer to three-dimensional systems, but are valid to some extent for two-dimensional systems as well. One of them relies on the assumption that strong disorder amplifies the Coulomb repulsion between electrons, giving rise to an increase in the pseudopotential  $\mu^*$  and, correspondingly, to a reduction in  $T_c^{(2)}$  (Refs. 61 and 62). It has been shown for t .ree-dimensional superconductors<sup>61</sup> that this effect is seen only for  $\lambda \sim 1$ , and is due to the reduction in the diffusion coefficient D of electrons near MIT. The pseudopotential  $\mu^*$  then becomes a function of  $\rho$ , which enables us to use the McMillan formula (3.3) to calculate the reduction in  $T_c$  with increasing  $\rho$ . The results of calculations are in qualitative agreement with the behavior of compounds with the A15 lattice. However, tunneling experiments with Nb<sub>3</sub>Sn have not revealed a significant increase in  $\mu^*$  with increasing  $\rho$  (Ref. 63).

There is one other possible pair-breaking mechanism in a system of interacting electrons that is due to the increase in spin fluctuations as the MIT is approached.<sup>42,64–67</sup> For example, it is noted in Ref. 64 that Coulomb correlations near the MIT lead to the appearance of a random spin density wave which reduces localized magnetic moments. The appearance of spin fluctuations is related in Refs. 42 and 56 to the effect of Coulomb repulsion which, as disorder increases, ensures that the system of interacting electrons becomes unstable with respect to transitions to the ferromagnetic state. These effects have been predicted for both two-dimensional and three-dimensional systems and, according to Refs. 42 and 66, the effect of spin fluctuations becomes perceptible not only for strong  $\lambda \sim 1$ , but also weak  $\lambda \ll 1$  disorder. For three-dimensional systems, the reduction in  $T_c$  under the influence of disorder is described<sup>66</sup> by the following expression, typical for gapless superconductivity:

$$\ln \frac{T_{c0}}{T_c} = \psi \left( \frac{1}{2} + \beta \right) - \psi \left( \frac{1}{2} \right), \qquad (3.6)$$

where  $\Psi$  is the digamma function,  $\beta = (9\sqrt{3}/2)\lambda^2(u/\eta)$ , u is the dimensionless constant representing the screening of the Coulomb interaction, and  $\eta^{-1}$  is the factor representing the enhancement of the static spin susceptibility in a system of interacting electrons (in the Hubbard model). For two-dimensional systems,

$$\ln \frac{T_{\rm c}}{T_{\rm co}} = -\frac{3}{4\eta} \pi^2 u \lambda C_2, \qquad (3.7)$$

where

$$C_{2} = \ln \frac{\hbar}{\pi k T_{c} \tau}, \quad \eta \ll \frac{\tau k T_{c}}{\hbar} \ll 1,$$
$$= \left(\frac{2}{3\pi^{2}}\right)^{3} \ln^{3} \frac{\hbar}{\pi k T_{c} \tau}, \quad \frac{\tau k T_{c}}{\hbar} \ll \eta \ll 1$$

It is interesting to note that, for weak disorder  $\lambda \leq 1$ , the expression given by (3.7) is in agreement, as is (3.5), with the experimental results given by (3.4) for thin films. However, a sufficiently reliable direct confirmation of the amplification of spin fluctuations near MIT is still lacking.

The BCS model was used in Ref. 62, 68 and 69 to examine the behavior of three-dimensional and quasi-two-dimensional superconductors near the mobility threshold for the Anderson transition. The GL equations were used under the conditions of strong  $(\lambda \sim 1)$  disorder, taking into account the scaling of the diffusion coefficient D near the MIT. It is shown within the framework of this approach that an increase in disorder is accompanied by a significant increase in the role of thermodynamic fluctuations near  $T_c$ . The effect of these fluctuations can lead to a reduction in  $T_c$ . For the three-dimensional case, we have<sup>69</sup>

$$\frac{T_{\rm c}}{T_{\rm c0}} = 1 - 0.48 \frac{\rho}{\rho_{\rm m}} \frac{kT_{\rm c0}}{E_{\rm F}}$$
(3.8)

where  $\rho_m$  is the maximum metallic resistivity according to Mott.<sup>1</sup> This formula is of limited utility because it is valid only near MIT. One interesting prediction of this approach<sup>62,68,69</sup> is that superconductivity will persist after the transition to the dielectric  $\xi_i$ ,  $\xi_i \ge (N(E_F)kT_c)^{-1/3}$ , i.e., close enough to the mobility threshold. It is therefore considered that the insulator-superconductor transition can be observed as the temperature is reduced.

To conclude this Section, let us consider the effect on the critical point  $T_c$  of phase or inelastic relaxation of electrons due to different types of inelastic interaction between quasiparticles. These processes ensure the attainment of equilibrium between the quasiparticles and the Cooper pairs (creation and recombination of pairs).<sup>70</sup> When the disorder is weak, the characteristic phase relaxation time  $\tau_{\varphi}$  play a significant part in the effect of weak localization and fluctuation superconductivity above  $T_c$  (Refs. 4 and 5). For example, they determine the size of the Maki-Thompson fluctuation correction.<sup>71,72</sup> In the latter case, phase and inelastic relaxation leads to the breaking of fluctuation Cooper pairs. The numerical parameter representing this pair-breaking mechanism is  $\delta = \ln(T_{c0}/T_c) \approx (T_{c0} - T_c)/T_c$ , where  $T_{c0}$ is the unperturbed value of  $T_c$ , and <sup>50,73</sup>

$$\delta = \frac{\hbar}{8kT\tau_{\varphi}} . \tag{3.9}$$

The effect of phase and inelastic relaxation on the superconducting properties is amplified as disorder increases (Refs. 26, 73–76). This has been demonstrated experimentally in Sec. 2 of Ref. 26: the enhancement of inelastic relaxation of electrons leads to the spreading of the superconducting gap (Fig. 4 and 5) and gapless superconductivity is established. This type of effect of inelastic processes can be postulated on the basis of general considerations involving the uncertainty principle (Ref. 70, p. 291). The Abrikosov-Gor'kov theory of gapless superconductivity (see the presentation in Ref. 70) leads to the following well-known expression for the reduction in  $T_c$  under the influence of different pairing factors:

$$\ln \frac{T_{\rm c}}{T_{\rm c0}} = \psi \left(\frac{1}{2}\right) - \psi \left(\frac{1}{2} + \frac{\hbar/\tau_{\rm p}}{4\pi k T_{\rm c}}\right), \qquad (3.10)$$

where  $\tau_p$  is the characteristic time for the breaking up of pairs. For example, when magnetic impurities are present,  $\tau_p$  is identical with the spin-spin relaxation time  $\tau_s$ .

Several recent publications<sup>73-76</sup> have examined the contribution of phase and inelastic relaxation of electrons to the breaking up of pairs in disordered systems. According to Ref. 75, phase relaxation becomes enhanced near MIT and produces a considerable contribution to the suppression of superconductivity. Theoretical and experimental studies in the case of weak disorder (Refs. 4, 5, 74 and 77–79) are also found to support the enhancement of phase relaxation with increasing disorder. For example, for two-dimensional systems,<sup>4</sup> the phase relaxation time due to electron–electron collisions with small momentum transfers is described by

$$\tau_e^{-1} = \frac{\pi kT}{\hbar} \lambda \ln \frac{1}{2\pi\lambda} , \qquad (3.11)$$

i.e.,  $\tau_e^{-1} \sim R_{\Box}$ . Near  $T_c$ , this time is modified to become  $\tau_{es} = \tau_e \gamma$  (Ref. 74), where the factor  $\gamma$  represents the recombination of feetorms into superconducting pairs, but, in this case,  $\tau_{es}^{-1} \sim R_{\Box}$ . The contribution of inelastic electron-phonon collisions during phase relaxation is represented by the time  $\tau_{ep}$ , for which  $\tau_{ep}^{-1} = (\pi^2/2) (kT)^2 / mMc_T^3 l$  in the case of highly disordered and amorphous systems, where *m* and *M* are, respectively, the electron and ion masses, and  $c_T$  is the transverse sound velocity. Thus, phase relaxation due to EEI and EPI is speeded up as disorder increases.

The validity of (3.10) with  $\tau_{\rho} = \tau_{\varphi}$  in the case of disordered systems was discussed in Refs. 44 and 74. Formula (3.9) is then a special case of (3.10) when  $\delta \leq 1$ . When (3.11) is used for  $\tau_{\varphi}$ , and we have a low degree of disorder  $(R_{\Box} \leq 1 \text{ k}\Omega)$ , we can show that,  $\delta \approx 10^{-4} R_{\Box}$ , which agrees with the experimental results (3.4) for weakly disordered films. Formula (3.10) has been used in the case of stronger disorder in amorphous films of bismuth with  $R_{\Box}$  up to about 6 k $\Omega$  (Ref. 79). The experimental function  $T_c(R_{\Box})$  was found to be satisfactorily described by (3.10) for different interpretations of  $\tau_{es}$  (Ref. 74) and  $\tau_{ep}$  (Ref. 75) (Fig. 9).



FIG. 9. The function  $T_c(R_{\Box})$  for an amorphous Bi film.<sup>79</sup> The curves are drawn in accordance with (3.10) for  $\tau_p^{-1} = 2\tau_{es}^{-1}$  (1) and  $\tau_p^{-1} = \tau_{es}^{-1} + \tau_{ep}^{-1}$  (2).

We note in conclusion that the pair-breaking effect of inelastic and phase relaxation is still a controversial topic (see the discussion in Ref. 80), so that further theoretical and experimental studies are necessary in this area. In addition, there is an urgent need for experimental studies of spin effects (Refs. 42 and 64–67) and thermodynamic fluctuations in the order parameter<sup>62,68,69</sup> near the MIT. They should enable us to identify the more important mechanisms responsible for the suppression of suprconductivity under the conditions of strong disorder.

3.1.2. Heterogeneous systems. The properties of heterogeneous systems have recently attracted considerable attention. Three types of heterogeneous structure can be identified in the case of films, namely (1) disordered mixture of metal and dielectric, (2) granulated films consisting of roughly equal granules (of size  $\sim 10$  nm) in a dielectric host, and (3) discontinuous or, in the limit, island films.

The properties of disordered mixtures of a metal and a dielectric are largely determined by classical percolation effects (Ref. 2). Such systems are characterized by the correlational percolation length  $\xi_{\rm p}$ , which corresponds to the largest percolation clusters in the dielectric region, As the volume fraction x of the metallic component increases, the percolation length is found to increase and tends to infinity as  $x \rightarrow x_{cp}$  (i.e., an infinite cluster is formed). The effects of weak and strong localization of electrons in percolation systems are taken into account in Refs. 24, 81, and 82. It is shown in Ref. 24 that the Anderson transition can occur for  $x = x_c \gtrsim x_{cp}$ . The suppression of superconductivity due to localization is governed by the ratio (for  $x = x_c$ ) of the lengths  $\xi_p$  and  $\xi_l$  (localization length). When  $\xi_l/\xi_p \ll 1$ , the conductivity is determined exclusively by percolation effects. In that case,  $x_c - x_{cp} \ll 1$  and the effect of localization on  $T_c$  is seen only at the percolation threshold  $x_{cp}$  (see the discussion of Fig. 3 in Sec. 2). When  $\xi_l/\xi_p \ge 1$ , the reduction in  $T_c$  under the influence of localization can manifest itself far from the percolation threshold for  $x_{cp} < x < x_c$ . Estimates of the shift in  $T_c$  near the percolation threshold are given in Ref. 83. The problem as a whole is still far from resolution.

(a) the energy level separation in an individual granule:

$$\delta E \approx (d^3 N(E_{\rm F}))^{-1} \tag{3.12}$$

where d is the granule diameter.

(b) The energies  $\hbar\omega_t$ , where  $\omega_t$  is the frequency of electron hops between granules and  $\omega_t^2$  is related to the tunneling probability *P* 

$$P \sim \omega_t^3 \sim e^{-2\chi_s} \tag{3.13}$$

where s is the thickness of the dielectric between the granules,  $\chi = \hbar^{-1} (2m\varphi_0)^{1/2}$ , m is the electron mass,  $\varphi_0$  is the effective height of the potential barrier, and  $\chi^{-1}$  is the decay constant of the wave function in the dielectric.

(c) The charging energy  $E_c$ , necessary to transfer an electron from one neutral granule to another with the formation of a pair of oppositely charged granules:

$$E_c \approx \frac{e^a}{d\kappa} \approx \frac{e^a}{2C}$$
 (3.14)

where  $\kappa$  is the dielectric constant and C the capacitance of the granules.

(d) The thermal energy  $\sim kT$ .

(e) The Josephson coupling energy between the granules

$$E_{j} = \frac{\pi\hbar}{4e^{2}R_{\rm N}} \Delta(T) \, \text{th} \, \frac{\Delta(T)}{2kT} \,, \qquad (3.15)$$

in which  $\Delta(T)$  is the superconducting gap, T is the temperature and  $R_N$  is the tunneling resistance between the granules, where

$$\frac{1}{R_{\rm N}} = \frac{e^{\rm a}}{\hbar} \frac{\hbar\omega_t}{E_{\rm a}} \,. \tag{3.16}$$

The energy  $E_a$  is the characteristic level misalignment energy in neighboring granules and may be determined by level splitting in small granules, charging effects, and other factors.<sup>22,84-86</sup>

Quantum mechanical tunneling occurs between states of equal energy. The level mismatch between neighboring granules has a slight effect on conductivity for low barriers (small s) or high temperatures for which  $\hbar\omega_i, kT \ge E_a$ . Electrons in the granulated metal then propagate relatively freely by nonactivated tunneling. For low enough temperatures  $(E_j \ge kT)$ , global phase coherence is established in such systems by Josephson coupling between granules. In the general case, the properties of granulated metals with low barriers are similar to those of homogeneous dirty metals.

The heterogeneity of the granulated metal becomes significant for high enough barriers between the granules. As s increases, the energy level mismatch begins to have a significant effect on electron hops at low temperatures. The energy  $E_a$  necessary to compensate the level mismatch is then acquired by thermal activation. Tunneling becomes activated, and its probability is given by

$$P \sim e^{-2\chi_s} e^{-E_a/kT}$$
 (3.17)

For granulated films, the transition to activated conductivity occurs for  $R_{\Box} \gtrsim 20-30 \text{ k}\Omega$  (Refs. 9 and 10) and assumes the hopping character. The properties of MIT and hopping conductivity in granulated metals have recently attracted considerable interest (see Refs. 10, 20, 27, 28, 82, and 87 and the references therein).

The enhancement of the localization of electrons in granules with increasing thickness of the dielectric medium between the granules is accompanied by a significant change in the superconducting properties of the granulated metal. First of all, we have to take into account the fact that level splitting in small granules can lead to the spreading of the superconducting gap and to the suppression of superconductivity. This factor can be neglected for large enough granules, for which  $\delta E \ll kT_c$ . In view of (3.12), this condition can be rewritten in the form<sup>85</sup>

$$d \gg d_0 = \left(\frac{1}{N(E_{\rm F})} kT_{\rm c}\right)^{1/3}$$
 (3.18)

where  $d_0 \approx 3$  nm for typical metals. Thus, for a coupled system of granules with  $d \leq d_0$ , an increase in s affects both the order parameter and the phase coherence of electrons. The superconducting properties of systems with  $d \gg d_0$  are determined in the first instance by the phase coherence between granules. For such systems, the superconducting transition often has the two-step character shown in Fig. 10. When the temperature is reduced, there is at first an appreciable reduction in resistance at  $T_{c0}$  that corresponds to the transition of the granules to the superconducting state. The final fall in resistance to zero occurs at a certain temperature  $T_c < T_{c0}$  after global phase coherence has been established between the granules by Josephson tunneling.

As the thickness s of the dielectric between the granules increases, i.e., as we approach the MIT, the global phase coherence is more difficult to establish with decreasing temperature, and this leads to a reduction in the observed  $T_c$ . This behavior is easy to understand qualitatively, but is diffi-



FIG. 10. Resistive junctions of two Sn-Ge films with  $R_{\Box} = 1.92 \ \Omega$  (1) and 2.08  $\Omega$  (2) for  $T = 4.2 \ K$  (Ref. 88).

cult to describe quantitatively for real granulated metals. This is so because, theoretically, it is difficult to take into account all the microstructural properties of real granulated metals, which are themselves usually poorly known. It is therefore common to employ various idealized models of the structure of granulated metals. The first approximation is usually taken to be the regular three- or two-dimensional lattice of granules of equal size, separated by a dielectric of constant thickness (this is the so-called XY model).89,90 According to Ref. 89, the characteristic effective coherence length  $\xi_{\text{eff}}(T)$  is much shorter than  $\xi_{\text{GL}}(T)$  (which corresponds to the properties of the granule material), but has the same temperature dependence. Granulated systems are classified in Ref. 89 as strongly bonded or weakly bonded, depending on whether  $\xi_{\text{eff}}(T) \ge d$  or  $\xi_{\text{eff}}(T) \ll d$  is satisfied. In the latter case, the system behaves like a set of zero-dimensional superconductors. The presence of the dielectric host ensures that the superconducting transition occurs at a certain temperature  $T_c < T_{c0}$ , where  $T_{c0}$  is the critical temperature of the granule material. The shift of  $T_c$ , represented by the quantity  $\delta = (T_{c0} - T_c)/T_c$ , increases with increasing s and decreasing d. Quantitative estimates of  $\delta$  for  $d \ge d_0$  and  $d \leq d_0$  are given in Ref. 89. At low temperatures, quantum phase fluctuations should play an important part in such systems and can destroy the phase coherence.84,90,91 This may lead to quasireentrant phenomena (Sec. 4).

In an ideal set of granules, e.g., in the XY model, phase coherence occurs simultaneously throughout the volume and the spreading of the resistive transition is determined exclusively by the influence of fluctuations in the order parameter. Real granulated metals usually have a spatial distribution of granule dimensions and thicknesses of the dielectric medium between the granules. The spread in the thickness s of the dielectric between the granules is particularly important because the tunneling probability is an exponential function of s [see (3.13) and (3.17)]. The percolation model of the superconducting transition is particularly attractive for such systems.<sup>92,93</sup> According to Ref. 92, as the temperature is reduced, phase coherence is established initially only in a limited number of superconducting clusters in which the condition  $E_i \gtrsim kT$  is satisfied for adjacent granules. As the temperature continues to fall, this condition is satisfied for an increasing number of adjacent granules, superconducting clusters grow, and an infinite cluster is formed at a certain temperature  $T_c < T_{c0}$ , i.e., the resistance of the system vanishes. This picture remains valid, at least qualitatively if, for sufficiently large mean values of s, the energy level mismatch between neighboring granules becomes more significant, and the Josephson coupling between them is established when the following more stringent condition is satisfied:

$$E_j \gtrsim kT + E_a. \tag{3.19}$$

If we consider that the level mismatch is determined exclusively by charging effects, we must put  $E_a = E_c$  in (3.19).<sup>93</sup> The percolation model provides a qualitative explanation of the reduction in  $T_c$  in granulated metals as the resistivity increases, and also the additional spreading of resistive transitions due to the influence of heterogeneity.

The main mechanisms responsible for the connection between disorder and  $T_c$  for heterogeneous systems have

now been identified. Real materials have typically a statistical spread of basic structural characteristics such as the dimensions and shape of superconducting regions, and the distribution of the dielectric material between them. This means that further and improved percolation and statistical calculations will be necessary. For granulated metals, there is an urgent need for a continuation of experimental studies of Josephson contacts between granules, and of hopping conductivity on the dielectric side of the MIT.

#### 3.2. Upper critical field H<sub>c2</sub>

# 3.2.1. Homogeneous systems

The upper critical magnetic field  $H_{c2}$  is very sensitive to disorder. For weakly disordered type II superconductors, the temperature dependence  $H_{c2}(T)$  is satisfactorily described by the theory of Werthamer, Helfand, and Hohenberg (WHH),<sup>94</sup> developed in the BCS approximation on the basis of the GL equations. The general and rather complicated WHH formula describes  $H_{c2}(T)$  and takes into account both the orbital pairing effect of the magnetic field and the contributions of the spin-orbit interaction and Pauli paramagnetism. When only the orbital effects are taken into account, the formula takes the form

$$\ln \frac{T}{T_{\rm c}} = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\hbar/\tau_H}{4\pi kT}\right) \tag{3.20}$$

 $(\tau_H^{-1} = 2DeH/c)$ . This expression is a special case of (3.10) which describes the reduction in  $T_c$  under the influence of pairing interactions that break the time-reversal symmetry. The expression given by (3.20) refers to three-dimensional superconductors or films in a perpendicular magnetic field. An important parameter of the WHH theory is the slope of the  $H_{c2}(T)$  curve at  $T = T_c$ :

$$\frac{dH_{c_2}(T)}{dT}\Big|_{T=T_c} = H'_{c_2}(T_c) = -\frac{4kc}{\pi eD} = -\frac{4}{\pi} kc\rho N (E_F).$$
(3.21)

It is clear from this that the experimental values of  $H_{c2}(T)$  can be used to determine the diffusion coefficient D or the density of states  $N(E_F)$ .

When the function  $H_{c2}(T)$  is examined, it is convenient to use the dimensionless critical field

$$h_{cs}(t) = \frac{H_{cs}(t)}{-(dH_{cs}/dt)_{t=1}}, \qquad (3.22)$$

where  $t = T/T_c$ . In this case, expression (3.20) corresponds to the universal curve  $h_{c2}(t)$  (dashed line in Fig. 11). When t = 0, this function becomes  $h_{c2}(t) \approx 0.693$  and its derivative for t = 0 and t = 1 is 0 and -1, respectively. Hence, it follows that  $h_{c2}(t)$  and, correspondingly, the function  $H_{c2}(T)$ in the WHH model always has negative curvature.

The WHH theory was developed for the BCS model and does not take into account the possible influence of EEI and EPI. For example, it is shown in Ref. 96 that, even for weak superconductors, the influence of EET and EPI can lead to a significant renormalization of the limiting Pauli field  $H_p \approx kT_c/\mu_B$ , where  $\mu_B$  is the Bohr magneton. This leads to renormalization of some of the parameters of the WHH theory. For strongly coupled superconductors,  $H_{c2}$  can be enhanced by EPI.<sup>97,98</sup> We shall return to this effect later.



FIG. 11. The function  $h_{c2}(t)$  for three films of amorphous Bi with the following values of  $R_{\Box}$  (in  $\Omega$ ): 0.2 (1), 0.36 (2), and 0.85 (3) (Ref. 95). The dashed curve represents the WHH theory.<sup>94</sup>

Experiment shows that greater disorder is accompanied both by a reduction in  $T_c$  and by a change in the behavior of  $H_{c2}(T)$  (Refs. 44, 59, 95, and 98–102). In particular, disordered semiconductors have typically higher values of  $H_{c2}$ for  $T \ll T_c$  as compared with the predictions of the standard WHH theory.<sup>94</sup> There is particular interest in observations of positive curvature of the  $H_{c2}(T)$  curves (Refs. 44, 95, and 102; Figs. 11 and 12), which are in complete disagreement with WHH. Thus, while at first the appearance of positive curvature of the  $H_{c2}(T)$  curves was explained exclusively by the influence of concentrational, structural, and other inhomogeneities in the samples,<sup>100</sup> it is now considered that this behavior is also typical for disordered homogeneous metals.

We now turn to theoretical research into the effect of disorder on  $H_{c2}$ . For weak disorder  $\lambda \ll 1$ , the inclusion of WLE and EEI<sup>3-5</sup> within the framework of the approach developed in Ref. 57, which had led to (3.5) for  $T_c$ , leads to the following expression for two-dimensional superconductors:<sup>103</sup>

$$\ln \frac{T}{T_{co}} = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\hbar/\tau_H}{4\pi kT}\left(1 - \lambda b\right)\right) - \frac{g\lambda}{2}b^2$$
$$-g\lambda b\left[\psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\hbar/\tau_H}{4\pi kT}\right)\right] - \frac{g\lambda}{3}b^3$$

$$-g\lambda b^{2}\left[\psi\left(\frac{1}{2}\right)-\psi\left(\frac{1}{2}+\frac{\hbar}{4\pi kT}\right)\right].$$
(3.23)

When  $\lambda = 0$ , this expression reduces to (3.20) and, when H = 0, it reduces to (3.5). It can be shown from (3.23) that

$$\dot{H}_{c2}(T_c) \approx -\frac{4ck}{\pi eD} (1 + \lambda b).$$
 (3.24)



FIG. 12. The functions  $H_{c2}(T)$  for films of In-InO of different composition with  $R_{\Box}(k\Omega) \approx 3.5(1), 4.6(2)$  and 5.65(3) at 10 K (Ref. 44). Film thickness ~ 10 nm in all cases.

Thus, an increase in disorder leads to an increase in the slope of the  $H_{c2}(T)$  curve at  $T = T_c$  [cf. (3.21)]. In addition, the theory of Ref. 103 predicts a positive curvature for the  $H_{c2}(T)$  curves as disorder increases. Qualitative agreement with Ref. 103 was reported in Refs. 59 and 102 at temperatures that were not too low. The effect of weak disorder on  $H_{c2}$  has also been considered in Ref. 104 for two-dimensional systems.

The theories of Refs. 103 and 104 are valid for weak disorder  $(\lambda \leq 1)$  and predict a considerable increase in  $H'_{c2}(T_c)$  in disordered systems. Several theories have been developed for strong disorder  $(\lambda \sim 1)$ . For example, the approach developed in Ref. 61 (Sec. 3.1.1-2) is used in Ref. 105 for three-dimensional superconductors and it is concluded that a magnetic field weakens localization of electrons and reduces the resistivity  $\rho$ , so that it should lead to a reduction in the Coulomb pseudopotential and a corresponding increase in  $T_c$ . This should lead to an increase in  $H_{c2}$  and a deviation of  $H_{c2}(T)$  from the WHH theory up to the appearance of positive curvature on these curves. The theory proposed in Ref. 105 is essentially based on the existence of negative magnetoresistance, and is capable of only qualitative comparison with experiment.

The WHH theory developed for the BCS model is probably not entirely valid for superconductors with strong EPI. Moreover, as shown above, EPI becomes stronger with increasing disorder, and has a considerable effect on  $T_c$ . It may be considered that strong EPI should affect the magnitude of  $H_{c2}$ , as well. The higher values, and the extension to lower temperatures, of the linear part of the function  $H_{c2}(T)$  of Pb- and Bi-based amorphous alloys was interpreted in Ref. 97 in terms of a modified WHH theory (strong spin-orbit interaction) that takes into account strong EPI in these alloys. According to Ref. 97, strong EPI should lead to a renormalization of the slope of the  $H_{c2}(T)$  curve at  $T = T_c$  as follows:

$$H'_{c2}(T_c) = -\alpha (1 + \lambda_{ep}) \frac{4kc}{\pi eD}, \qquad (3.25)$$

where  $\alpha \approx 1$  and  $\lambda_{ep}$  is the EPI constant [cf. (3.2)]. It is shown in Ref. 106 that, for superconductors with strong EPI, there is both an increase in  $H'_{c2}(T_c)$  and the  $H_{c2}(T)$ curve should have positive curvature for high enough  $\lambda_{ep}$ . According to Ref. 106,  $h_{c2}(0) \approx 0.45 \lambda_{ep}^{1/2}$  for  $\lambda_{ep} \ge 1$  so that  $h_{c2}(0) \gtrsim 1$  is obtained for  $\lambda_{ep} \gtrsim 4$ , i.e., we have positive curvature. This is in qualitative agreement with the experimental results in Ref. 95. The extension of the WHH theory to the case of strong EPI was reported in Ref. 107, but without taking into account localization effects. Further research will be necessary for a more complete understanding of the influence of EPI on  $H_{c2}$ , especially under the conditions of strong disorder ( $\lambda \sim 1$ ).

The behavior of  $H_{c2}$  (T) near the mobility threshold for the Anderson transition ( $\lambda \sim 1$ ) has also been examined in Refs. 62, 68, and 69 (they were mentioned above in connection with the effect of disorder on  $T_c$ ). In the standard theory of dirty superconductors, we have near  $T_c$ 

$$H_{c2}(T) = \frac{4ckT}{\pi De} \varepsilon = \frac{\Phi_0}{2\pi\xi_{GL}^2(T)},$$
(3.26)

where  $\Phi_0 = \pi c \hbar / e$  is the flux quantum and  $\varepsilon = \ln(T_c / T)$ . The GL coherence length is given by

$$\xi_{\rm GL}(T) = \xi_{\rm GL}(0) \, e^{-1/2}, \tag{3.27}$$

where  $\xi_{GL}(0) = (\pi D\hbar/8kT_c)$ . According to Ref. 62, the quantity  $\xi_{GL}^2(0)$  is given by the following expression if we are close enough to the mobility threshold (on the metal side of the MIT):

$$\tilde{\xi}_{GL}^{2}(0) \approx \xi_{GL}^{2}(0) (k_{F}\xi_{l})^{-1},$$
(3.28)

where  $\xi_l$  is the correlation length for the Anderson transition, given by (for three-dimensional systems)<sup>62</sup>

$$\xi_l = k_{\rm F}^{-1} \left| 1 - \frac{\sigma}{\sigma_{\rm c}} \right|^{-\gamma}, \tag{3.29}$$

where  $\nu \leq 1$  is the critical index,  $\sigma$  is the conductivity, and  $\sigma_c$ is the conductivity at the mobility threshold, whose order of magnitude is the same as that of the minimum metallic conductivity according to Mott<sup>1</sup> ( $\sigma_{\min} \approx e^2 k_F / \pi^3 \hbar$ ). The quantity  $\xi_1$  increases with increasing disorder, and this should lead to a reduction in  $\xi_{GL}(0)$  and to a corresponding increase in  $H_{c2}(T)$  and  $H'_c(T)$ . In addition, it has been shown<sup>62,68</sup> that the negative curvature of the  $H_{c2}(T)$  curve should become positive as the mobility threshold is approached. This is in qualitative agreement with the results reported in Ref. 95. Comparison of the experimental results with the theoretical data in Refs. 62 and 68 is impeded by the considerable uncertainties in  $\sigma_c$  and  $\nu$ .

Most experimental and theoretical papers concentrate on the increase in  $H_c$  and  $H'_{c2}(T)$  with increasing disorder. At the same time, as for  $T_c$ , the field  $H_{c2}$  should decrease when the disorder is strong enough, and this has, in fact, been reported in Ref. 44 (cf. Fig. 12). It follows from (3.21) and (3.26) that the reduction in  $H_{c2}$  may be related to the reduction in  $N(E_F)$  as the MIT is approached. However, these formulas are valid only for weak disorder (and, in any event, not near the MIT). The reduction in  $H_{c2}$  near MIT is examined in Ref. 69, but the problem as a whole is not treated there.

It is thus clear that experiments suggest that, as disorder increases, the behavior of  $H_{c2}(T)$  increasingly deviates from of the classical dirty superconductors. Many of these differences, for example, the positive curvature of the  $H_{c2}(T)$  curves have not as yet been satisfactorily explained. The effect of EPI on  $H_{c2}(T)$  and the reduction in this function near the MIT have not been adequately investigated, either. It is highly desirable to continue investigations into these questions.

#### 3.2.2. Heterogeneous systems

The effect of heterogeneity on the behavior of  $H_{c2}(T)$  has been examined experimentally for the following systems: (1) amorphous alloys with assumed presence of structural, concentrational, phase or other heterogeneity,<sup>100,101</sup> (2) granulated metals,<sup>108,109</sup> and (3) percolation systems (disordered mixtures of a metal and a dielectric or noncontinuous films).<sup>108-111</sup>

For amorphous alloys, the influence of heterogeneity has been used as a basis for the explanation of the higher values of  $H_{c2}(T)$  for  $T \ll T_c$ . It was then considered that the heterogeneity could be seen on a length scale of the order of  $\xi_{GL}(0)$  (~10 nm). Discussions of the observed deviations from the WHH theory and numerical calculations have been based on different models of statistical distributions of D,  $\sigma$ , and  $T_c$  (Refs. 100, 101, and 112). Calculations such as those reported in Refs. 100 and 112 are, however, merely simulations, because the precise character and scale of the heterogeneity of amorphous alloys are usually not known.

For granulated metals consisting of roughly equal granules, it is possible, in accordance with Sec. 3.1.2, to examine two limiting cases of  $H_{c2}$  (T). For small thicknesses s of the dielectric medium between the granules, the granulated metal behaves as an ordinary homogeneous dirty superconductor. The function  $H_{c2}$  (T) is then given by (3.20). Slight deviations from the WHH theory due to the WLE and EEI effects<sup>103</sup> are then possible. For large s, the Josephson coupling between the granules can be so reduced that they can be regarded as independent zero-dimensional semiconductors<sup>89</sup> (the condition for this is  $\xi_{GL}$  (T) > d. The magnetic pair-breaking time in (3.20) can then be written in the form:<sup>70</sup>

$$\tau_H = 0, \, \left[ \pi^2 \hbar D \left( \frac{H}{\Phi_0} \right)^2 d^2 \right]$$
(3.30)

where d is the granule diameter. It follows from (3.20) and (3.30) that near  $T_c$ ,

$$H_{c2} \sim (T_c - T)^{1/2}$$
. (3.31)

This behavior of the granulated metals was observed in Refs. 108 and 113. The behavior of the function  $H_{c2}(T)$  in the intermediate states between these limits of strong and weak Josephson coupling between granules has so far been investigated only superficially and is difficult to analyze theoretically. Some experimental results and theoretical considerations relating to this are given in Refs. 108 and 109.

Only general theoretical ideas are available at present on the behavior of  $H_{c2}$  (T) in percolation structures (disordered mixtures of a metal and a dielectric or discontinuous films). According to Refs. 109 and 111, the superconducting properties of such systems are determined by the ratio of two characteristic lengths, namely, the correlational percolation length  $\xi_p$  and the effective correlation superconductivity length  $\xi_{eff}$  (T) (which, in heterogeneous systems, plays the part of the coherence length  $\xi_{GL}(T)$ . For heterogeneous systems,  $\xi_{eff}(T) < \xi_p$ , we have  $H_{c2}(T) = \Phi_0/2\pi\xi_{eff}^2(T)$ , the form of which is the same as that of (3.26) but  $H_{c2}$  then has a different temperature dependence. In general, we have near  $T_c$ 

$$H_{\rm c2}(T) \sim \varepsilon_{\rm eff}^2(T) \sim (T_{\rm c} - T)^{\theta}, \qquad (3.32)$$

where the critical index is  $\theta = 1$  for homogeneous systems. For percolation systems,  $\theta < 1$  and, as the heterogeneity is enhanced and the dimensions of the superconducting clusters are reduced, the index  $\theta$  approaches 0.5. The case  $\theta = 0.5$  is (as shown above) characteristic of systems of weakly coupled granules or islands with dimensions  $d < \xi_{GL}(T)$  [cf. (3.31)]. The relation given by (3.32) with  $0.5 < \theta < 1$  has also been confirmed experimentally.<sup>95,108,109</sup> The significant point is that, when  $0.5 \leq \theta < 1$ , the function  $dH_{c2} dT \sim (T_c - T)^{\theta - 1}$  diverges as  $T \rightarrow T_c$ . Hence, if the  $H_{c2}(T)$  curve for three-dimensional samples (or films with a perpendicular field) approaches  $T_c$  with an infinite slope (Fig. 13), this is a definite indication that heterogeneity is affecting superconducting properties. The current level of understanding of the behavior of  $H_{c2}$  (T) for heterogeneous systems cannot be regarded as satisfactory. It can, however, serve as a good starting point for further investigations into this interesting question.

#### 3.3 Fluctuational conductivity above $T_c$

Let us begin with the fluctuation properties of two-dimensional systems in the case of weak disorder  $\lambda < 1$ . Fluctuational conductivity increases as we approach  $T_c$ , and depends on the ratio of the characteristic relaxation times of electrons, namely,  $\tau_{\varphi}$ , which represents phase relaxation,  $\tau_T = \hbar/kT$  (connected with EEI), and the time  $\tau_{GL}$  of relaxation of the order parameter:

$$\frac{1}{\tau_{\rm GL}} = \frac{8kT}{\pi\hbar} \varepsilon, \qquad (3.33)$$

where  $\varepsilon = \ln(T/T_c)$ . The time  $\tau_{GL}$  is related to  $\xi_{GL}(T)$  by  $\xi_{GL} = (D\tau_{GL})^{1/2}$  [cf. (3.27)]. We shall assume that quantum corrections to conductivity are significant<sup>4</sup>  $\tau_{GL}^{-1}, \tau_m^{-1}, \tau_T^{-1} \ll \tau^{-1}$ .

 $\tau_{GL}^{-1}, \tau_{\varphi}^{-1}, \tau_{T}^{-1} \ll \tau^{-1}.$ Near  $T_c$ , the fluctuational conductivity for  $\varepsilon \ll 1$  ( $\tau_{GL}^{-1} \ll \tau_{T}^{-1}$ ) is determined by the Aslamazov-Larkin (AL) correction<sup>114</sup> and the Maki-Thompson (MT) correction:<sup>71-72</sup>



FIG. 13. Temperature dependence of  $H_{c2}$  for an inhomogeneous In–Ge film, 200 nm thick ( $\rho_n = 5 \times 10^{-4} \ \Omega \text{ cm}$ ).<sup>109</sup>

$$\Delta\sigma_{\rm AL} = \frac{e^2}{16\hbar} \frac{1}{\epsilon}, \qquad (3.34)$$

$$\Delta \sigma_{\rm MT} = \frac{e^2}{8\hbar} \frac{1}{\varepsilon - \delta} \ln \frac{\varepsilon}{\delta} , \qquad (3.35)$$

where  $\delta = \ln(T_{c0}/T_c)$  and is determined by the time  $\tau_{\varphi}$  [cf. (3.9)]. The AL correction is related to the presence of fluctuational Cooper pairs and the MT correction is due to the interaction between quasiparticles and the fluctuational pairs. The AL correction predominates near  $T_c$  for  $\varepsilon \ll \delta(\tau_{GL}^{-1} \ll \tau_{\omega}^{-1})$ . If  $\varepsilon$  and  $\delta$  are of the same order, both corrections have to be taken into account. The contribution of the AL mechanism declines as we depart from  $T_c$ , whereas the contribution of the MT mechanism increases. The enhancement of phase relaxation with increasing disorder (increasing  $\tau_{ph}^{-1}$  leads to an expansion of the temperature region in which the AL corrections predominate.<sup>50</sup>

The expressions (3.34) and (3.35) are valid for  $\varepsilon$ ,  $\delta \leq 1$ . Well away from  $T_c$ , and when  $\varepsilon \gg \delta$ , the contribution of the AL correction can be neglected, whereas the MT correction can be written in the following form:<sup>115</sup>

$$\Delta \sigma_{\rm MT} = \frac{e^2}{2\pi^2 \hbar} \beta(T) \ln \frac{\tau_{\rm ph}}{\tau_T}.$$
(3.36)

The function  $\beta(T)$  increases as we approach  $T_c$ :  $\beta(T) \sim 1/\varepsilon^2$  for  $\varepsilon \gg 1$  (Ref. 115). Formula (3.36) was derived on the assumption that  $\tau_{ph}^{-1} \ll \tau_T^{-1}$ , i.e., that the quasiparticle description of the theory of the Fermi fluid was valid.<sup>4</sup> The derivation of the general expression for the MT correction is valid in a wide temperature range above  $T_c$ , and the inclusion of the strong influence of phase correlation (for  $\tau_{ph}^{-1}$  and  $\tau_T^{-1}$  of the order of unity) is reported in Refs. 116 and 117.

It is shown in Refs. 4, 117, and 118 that, when  $\varepsilon \gg \delta$ , we have to take into account both the MT correction and the socalled Cooper correction (associated with the change in the density of states in the disordered systems as a result of the effect of EEI). The latter correction has the typical temperature dependence  $\Delta \sigma_c \sim \ln \varepsilon$ . According to Refs. 4 and 118,

$$\Delta \sigma_{\rm C} = -\frac{e^2}{2\pi^2 \hbar} \ln \frac{\ln \left( \hbar/kT_{\rm c} \tau \right)}{\epsilon} \,. \tag{3.37}$$

The Cooper correction has the opposite sign as compared with the AL and MT corrections. Its relative contribution to the fluctuational conductivity increases as we depart from  $T_c$  and extends to  $\varepsilon \ge 1$ . The influence of the Cooper correction on the conductivity of disordered films was noted in Refs. 119 and 120 for  $T \ge T_c$ .

The functions given by (3.34)-(3.37) are valid for weak disorder. The change in the fluctuational conductivity as the MIT is approached has been investigated to a much lesser extent than  $T_c$  and  $H_{c2}$ . General considerations suggest that stronger disorder should enhance the contribution of the Cooper correction (for  $T \gg T_c$ ). It may also be considered that the enhancement in phase relaxation as the MIT is approached<sup>26,73-76</sup> leads to a reduced contribution of the MT correction and to an expansion of the region of influence of the AL correction. This behavior was observed in Ref. 79.

The pair-breaking influence of phase and inelastic relaxation of electrons (Sec. 3.1.1-2) can have an appreciable influence<sup>121</sup> on the fluctuational conductivity for  $\varepsilon \gg \delta$  when  $\delta$  is temperature-dependent. It follows from (3.9) that  $\delta \sim T^{p-1}$  (where p in the expression  $\tau_{ph}^{-1} \sim T^{p}$  is an integer). The exponent p is often found to exceed unity. For example, p = 2, 3, or 4 for different types of relaxation due to EPI.<sup>77,79</sup> In such cases,  $\delta$  is found to increase with increasing temperature, and this produces a reduction in  $T_c$  [see (3.9) or (3.10)] and a corresponding increase in the effective value of  $\varepsilon = \ln(T/T_c(T))$  ( $T_c$  becomes a function of temperature). This may lead to an additional reduction [as compared with that expected by using (3.34)-(3.37)] in the fluctuational conductivity with increasing temperature (see the discussion and probable observation of this effect in Ref. 79).

For amorphous metals with a very short elastic scattering length for electrons, the following phenomenon, that is undoubtedly connected with the influence of disorder, has been observed. It was found that the temperature dependence of fluctuational conductivity  $\Delta \sigma_{\rm fl}(\varepsilon)$ , typical for the AL mechanism, was satisfied only up to  $\varepsilon^* \approx 0.05$ -0.1. This effect was observed both for three-dimensional<sup>122,123</sup> and the two-dimensional systems.<sup>79</sup> For  $\varepsilon \gtrsim \varepsilon^*$ , it was shown that  $\Delta \sigma_{\rm fl}(\varepsilon)$  was described by  $\Delta \sigma_{\rm fl} \approx \exp(-\varepsilon/\varepsilon_0)^{1/2}$  for threedimensional systems and  $\Delta \sigma_{\rm fl} \approx \exp(-\varepsilon/\varepsilon_0)$  for films. The quantity  $\varepsilon_0$  was found to lie between 0.1 and 0.4. This means that, for  $\varepsilon > \varepsilon^*$  there was an accelerated (as compared with the AL theory) reduction in  $\Delta \sigma_{\rm fl}$  with increasing temperature not too far from  $T_c$ . An acceptable explanation of this effect is still lacking (see the discussion in Ref. 79).

The AL correction for two-dimensional systems does not explicitly depend on the degree of disorder. However, for three-dimensional systems, we have  $\Delta \sigma_{AL} \sim 1/\xi_{GL}(T)$ . In view of the predicted<sup>62,68,69</sup> reduction in the coherence length as we approach the MIT [see (3.28)], we may expect, in this case,<sup>68,124</sup> an enhanced influence of fluctuations and an expansion of the region of strong fluctuations near  $T_c$ (Ginzburg region). This means that the superconducting transition in a disordered system near the MIT should be analogous to the  $\lambda$ -transition in liquid helium.<sup>68</sup> Near the mobility threshold, the fluctuational conductivity should also be strongly affected by spatial fluctuations in the order parameter.<sup>125</sup> These expected effects near the MIT have not as yet been investigated experimentally.

In heterogeneous systems (see Sec. 2.1.2), superconductivity is initially established with decreasing temperature only in a limited number of local regions between which there is no phase coherence (this is local superconductivity). The interval between the temperature at which the local superconductivity appears and the temperature at which global phase coherence is established over the entire disordered system depends on the degree of heterogeneity. When the latter is high enough, global phase coherence may be absent even for T = 0. This gives rise to a significant spreading of the resistance curves for the superconducting transition.

The function R(T) for diffuse superconducting transitions in granular metals was simulated in Ref. 126 by means of the percolation model.<sup>92</sup> It was assumed that the granulated metal consisted of roughly equal granules whose dimensions satisfied (3.8), but with a considerable spread of the thickness of the dielectric medium between the granules. The shape of the R(T) curve in this model depends significantly on the assumed statistical spread of the tunneling resistance between the granules [see (3.36)], which is difficult or even impossible to determine experimentally. Qualitative agreement with Ref. 126 was demonstrated for Sn-Ge films in Ref. 88.

Heterogeneity can also be responsible for the change in the dimensions of superconducting fluctuations (the socalled crossover) for  $T > T_c$ . Let us elucidate this effect in the case of granular metals. According to Ref. 89, a granular metal with roughly equal granule dimensions d behaves as a homogeneous medium for  $\xi_{\text{eff}}(T) \ge d$ , where  $\xi_{\text{eff}}$ .  $(T) = \xi_{\text{eff}}(0)\varepsilon^{-1/2}$  is the effective coherence length. In this case, the expression given by (3.34) is valid for the fluctuational conductivity of films when  $\varepsilon \ll 1$ . When  $\xi_{\text{eff}}(T) \le d$ , the system behaves as a set of weakly coupled zero-dimensional superconductors (Secs. 3.1.2 and 3.2.2) for which the fluctuational conductivity is given by<sup>89</sup>

$$\frac{\Delta\sigma_{\rm fl}}{\sigma_{\rm n}} = \left(\frac{\varepsilon_{\rm co}}{\varepsilon}\right)^2,\tag{3.38}$$

where  $\sigma_n$  is the normal conductivity,  $\varepsilon_{c0} = (d_0/d)^{3/2}$  is the critical Ginzburg region for zero-dimensional superconductor, and  $d_0$  is given by (3.18). Since  $\xi_{\text{eff}}(T)$  decreases as the temperature departs from  $T_c$ , one may expect that, for  $\varepsilon \approx \varepsilon_t = \xi_{eff}^2(0)/d^2$  there will be a change in the temperature dependence of the fluctuational conductivity,  $\Delta \sigma_{\rm fl}(\varepsilon)$ . When  $\varepsilon \ll \varepsilon_1$ , the fluctuational conductivity of films should satisfy (3.34), i.e.,  $\Delta \varepsilon_{\rm fl} \sim 1/\varepsilon$ , whereas for  $\varepsilon \gtrsim \varepsilon_{\rm r}$ , there should be a transition to  $\Delta \sigma_{\rm fl} \sim 1/\epsilon^2$ . This type of transition was predicted in Ref. 89 and experimentally confirmed in Ref. 127. It has been found<sup>113</sup> that the quantity  $\varepsilon_i$  for granulated In films was reduced by a magnetic field (Fig. 14) but  $\varepsilon_{c0}$  was increased, i.e., the field compresses the temperature region in which two-dimensional fluctuations are present, in agreement with the change in the size of fluctuations in a magnetic field by two units, as predicted in Refs. 128 and 129.

It is clear from the foregoing that the considerable advances made in recent years in fluctuational conductivity of disordered systems have been due to the advances in the theory of WLE and EEI (Refs. 3-5, 115, and 118), i.e., in the case of weak disorder. Studies of fluctuational conductivity for sufficiently strong disorder near the MIT have only just begun and remain very topical.

# 4. REENTRANT PHENOMENA IN THE SUPERCONDUCTIVITY OF HETEROGENEOUS SYSTEMS

It was shown above that a departure from the global phase coherence of electrons in heterogeneous systems consisting of weakly coupled superconducting regions gives rise to the suppression of effective superconductivity. The competition between superconductivity and localization of electrons in such systems can lead, under certain definite conditions, to a return from superconducting to the normal state as the temperature is reduced. This effect was first examined theoretically for granulated metals in Refs. 84 and 91. It was observed experimentally for the first time in Ref. 130, well before the emergence of the above mentioned theories. It was observed subsequently frequently for granulated<sup>22,44,45,131-132</sup> and island<sup>9,26,29-31,134,135</sup> films.

Reentrant phenomena are seen as minima in resistance for  $T < T_{c0}$ , where  $T_{c0}$  is the critical temperature of the homogeneous material and the resistance at a minimum does not usually fall to zero (this is why the effect is often called quasireentrant). Among existing experimental investiga-



FIG. 14. Effect of a perpendicular magnetic field on the fluctuational conductivity of a granulated In film above  $T_c$ . (Film thickness approximately 7 nm).<sup>113</sup> The experimental points correspond to H = 0 (1) and 36 (2) kOe. The slopes of the straight lines represent the functions  $\Delta\sigma_n \sim 1/\varepsilon_H$  and  $\Delta\sigma_n \sim 1/\varepsilon_H^2$ . Arrows show  $\varepsilon_H$  corresponding to the change in the dimension of fluctuations.

tions, we particularly emphasize those in which the strength of the Josephson coupling between the granules or islands was controlled in some particular way.<sup>29,130,133</sup> This meant that it was often possible to follow the appearance and evolution of reentrant effects in the transition from a homogeneous metal to a heterogeneous insulator (consisting of completely isolated superconducting granules or islands). This was done in Ref. 29 by a controlled variation of the mean thickness of ultrathin films (Fig. 15), whereas, in Ref. 133, the analogous effect was achieved by varying the potential difference V applied to a granulated film (Fig. 16).

The possibility of reentrant effects in granulated metals was examined theoretically in Refs. 84, 90, 91, and 136-140 with particular reference to the regular lattice of granules with equal potential barriers. If the basic reason for the mismatch between the energy levels of adjacent granules is the charging energy  $E_c$  [see (3.14)], global phase coherence should be established in such systems at sufficiently low temperatures for  $E_i > E_i^c = E_c/z$ , where z is the number of nearest neighbors. It has been shown (Refs. 90, 91, 136-140) that reentrant effects are possible for systems with  $E_i \approx E_i^c$ when charge and phase fluctuations are taken into account in different ways. For two-dimensional systems<sup>136,138,139</sup> reentrant effects can be related to the influence of thermally excited vortex-antivortex pairs (the Kosterlitz-Thouless-Berezinskii effect<sup>141,142</sup>). The results reported in Refs. 90, 91, and 136-140 are very sensitive to disorder (i.e., to spatial fluctuations in the dimensions of granules and the tunneling resistance  $R_N$  between them), so that, as noted in Ref. 31 and 90, it is very unlikely that they are valid for real granulated metals.

The properties of real granulated metals are in closer agreement with theory.<sup>84,126</sup> Quasiparticle tunneling, which can compensate the influence of charging energy for  $T \neq 0$ , was taken into account in Ref. 84. This effect and the reen-



FIG. 15. Change in the function  $R_{\Box}(T)$  for cold-deposited Ga films for a step change in the mean thickness in steps of 0.05–0.1 Å (Ref. 29).

trant mechanism that follows from it can be described qualitatively in terms of the uncertainty principle for the number N of quasiparticles in a granule and phase  $\varphi$ :

$$\Delta N \cdot \Delta \varphi \geqslant 1. \tag{4.1}$$



FIG. 16. The function  $R_{\Box}(T)$  for a granulated In film<sup>133</sup> for different values of applied voltage V: 10 (1) 5 (2), 2(3), 1 (4), 0.6 (5), 0.4 (6), 0.3 (7), 0.2 (8), 0.1 (9), and 0.04 (10). Insert shows  $R_{\Box}(T)$  for V = 0.5 V and different values of the perpendicular magnetic field H in kOe: 0 (1), 3.2 (2), 6.5 (3), 13 (4) and 44.5 (5). Film dimensions: length—3.4 nm, width—2 nm, thickness—approximately 6 nm.

If  $E_c$  is of the same order as  $kT_{c0}$ , the granulated metal will not exhibit activation-type conductivity for  $T \gg T_{c0}$ . As the temperature is reduced, the condition  $E_i > E_c + kT$  can be satisfied for all adjacent granules [cf. (3.19)], and global phase coherence of electrons is established in the system. Further reduction in temperature then ensures that the condition  $E_C \gg kT$  will begin to be satisfied and this will signify a transition to activation-type tunneling of single-particle excitations. In accordance with (3.17), the probability of this type of tunneling decreases exponentially with decreasing temperature, which, according to (4.1), leads to a reduction in  $\Delta N$  with increasing  $\Delta \varphi$ , i.e., to a departure of the phase coherence of electrons between granules. This departure of phase coherence of electrons in adjacent granules under the conditions of a considerable reduction in the number of unpaired electrons in the superconducting granules with decreasing temperature signifies a transition of the granulated metal to the dielectric state. According to Ref. 84, therefore, the following behavior is possible for granulated metals with  $E_i \approx E_c$ : for  $T > T_{c0}$ , the granulated metal behaves as an ordinary metal but, as the temperature is reduced, it undergoes a transition to the superconducting state; however, for  $T \ll T_{c0}$ , it becomes an insulator i.e., we have the superconductor-insulator transition.

Under the conditions of complete suppression of Josephson coupling between granules  $(E_c \gg E_j)$ , there is a significant change in the very character of the activated conductivity because of the appearance of the superconducting gap  $\Delta(T)$  in the electron spectrum.<sup>84</sup> This gap can play the part of the dielectric gap. According to Ref. 84, there are two mechanisms for activation-type conductivity under these conditions, namely, activated tunneling of Cooper pairs and single-particle excitations with activation energies of  $\sim E_c$ and  $\sim \Delta(T)$ , respectively. The dominant contribution to conductivity is provided by the mechanism with the lower activation energy. When  $E_c \gg \Delta(T)$ , the main contribution should be due to the hopping of one-electron excitations which, for  $T \ll T_{c0}$ , determines the function R(T):

$$R(T) \sim e^{\Delta(0)/kT},\tag{4.2}$$

where  $\Delta(0)$  is the gap at T = 0.

Reentrant effects in granulated metals are discussed in Ref. 126, bearing in mind (in accordance with the percolation model<sup>92,93</sup>) the statistical spread in the sizes of the granules and the thickness s of the dielectric medium between them, typical for real granulated metals. The spread in the values of s is particularly significant for the establishment of the phase coherence of electrons in granulated metals, since the tunneling probability and, correspondingly,  $E_i$ , are exponential functions of s [cf. (3.13) and (3.15)]. We shall follow Refs. 92, 93, and 126 and examine a model granulated system consisting of similar granules with a given distribution of values of s. Let  $s_m$  be the statistical average of the values of s. An increase in  $s_m$  brings the system closer to the MIT. When  $s_m$  is high enough, the system must be in a state in which a reduction in the temperature below  $T_{c0}$  produces the Josephson coupling for only a certain number of uncoupled superconducting clusters. The formation and growth of these clusters with decreasing temperature<sup>92,93</sup> leads to a reduction in resistance, but these clusters cannot "short" the entire system even for T = 0 when the spread in the value of s

is large enough (i.e., an infinite cluster is not formed). The minimum of R(T) may be due to an increase in the resistance of "unshorted" parts of the system with activation-type conductivity. However, as the temperature is reduced, the Josephson tunneling may also be suppressed<sup>84</sup> within the superconducting clusters.

The principal results of Refs. 84 and 126 have been confirmed at least qualitatively (and, in some cases, quantitatively) in Refs. 22 and 133, in which granulated In films were examined for reentrant effects in an applied voltage Vand a perpendicular magnetic field H. The samples had roughly equal granules (diameter approximately 6 nm) but different values of  $s_m$ . The experimental functions R(T, V,H) mirrored the competition between Josephson and activation-type tunneling. For example, the strong reduction in Rwith increasing V (cf. Fig. 16) is due to the reduction in the height of the potential barrier between the granules. In accordance with (3.13), this produces greater tunneling probability and reduces the localization of electrons in the granules which, in turn, leads to an enhancement of the phase coherence of electrons in adjacent granules. Hence, the resistance minimum (Fig. 16) that is associated with the superconductivity is found to appear as V increases. The magnetoresistance is then positive, and a strong enough magnetic field will completely suppress the resistance minimum (see insert in Fig. 16). The magnetic field will therefore suppress the Josephson tunneling between the granules. Further increase in V is accompanied by a considerable increase in the current I flowing through the film which, in turn, reduces superconductivity effects: the minimum is smoothed out and disappears, and the positive magnetoresistance is reduced. We note that an increase in V produces an effect that is analogous to that described in Refs. 29-31, whereby there is an increase in the effective thickness of island films (Fig. 15), which also facilitates an enhancement of Josephson coupling between islands.

The competition between localization and superconductivity is also noted in Ref. 22 in the case of the transition from positive to negative magnetoresistance as V was reduced, H increased, and temperature reduced. In all cases, this was due to the suppression of Josephson tunneling. The effect of the reduction in temperature is in agreement with the Efetov mechanism mentioned above.<sup>84</sup> For samples in which the Josephson tunneling between granules is completely suppressed, the transition of the granules to the superconducting state has a significant effect on the temperature dependence and the mechanism of hopping conductivity. When  $T < T_{c0}$ , it was found that  $R(T) \sim \exp(1/T)^{1/2}$  (Fig. 17), which corresponded to the effect of the Coulomb gap.<sup>2</sup> When  $T < T_{c0}$ , the resistance increased much more rapidly with reducing temperature and, for  $T \ll T_{c0}$ , the function R(T) could be described by  $R(T) \sim \exp(E/kT)$  where the energy E was approximately equal to the gap  $\Delta(0)$  of the cold-deposited In films. In accordance with Ref. 84, therefore, hopping conductivity is described by (4.2) for  $T \ll T_{c0}$ . The more rapid variation of R(T), observed when weakly coupled granules undergo a transition to the superconducting state, was noted earlier in Refs. 9, 130 and 143. According to the two-fluid treatment,<sup>143</sup> this is due to the reduction in the number of normal electrons in granules when a fraction of them undergo a transition to the superconducting state. When Josephson tunnel-

ing is suppressed, and the conductivity is determined exclusively by activated hopping of unpaired electrons, this leads to an additional increase in resistance for  $T < T_{c0}$ . A magnetic field suppresses the superconductivity of granules, and this is the reason for the observed anomalously high negative magnetoresistance for  $T < T_{c0}$  (Refs. 22 and 130; cf. Fig. 17). Allowance for the zero-dimensional character of the superconductivity of isolated granules [cf. (3.20) and (3.30)] was used in Ref. 22 together with (4.2) to achieve a complete description of the temperature and magnetic-field dependence of negative magnetoresistance for  $T \ll T_{c0}$ , i.e.,  $\ln(R(H)/R(0)) \sim -H^2/T$ . We may therefore conclude that the basic features of reentrant phenomena in granulated metals can be understood in terms of the theories proposed in Refs. 84 and 106, although we cannot totally exclude the influence of other possible reentrant mechanisms (see, for example, Ref. 144).

Our discussion of quasireentrant phenomena in granulated metals has so far concentrated on granule charging effects. It has been shown in recent years<sup>34-41</sup> that analyses of the effects of disorder on the superconductivity of granulated metals must take into account dissipative processes associated with the normal current flowing between the granules. This current may be due to quasiparticle tunneling and (or) the presence of normal shorting bridges between granules. The dissipative processes associated with the normal current can suppress quantum phase fluctuations and thereby significantly influence the establishment of global phase coherence. Dissipation is usually taken into account within the framework of the resistive model of the Josephson contact (resistively shunted junction model; cf. Refs. 32 and 33). According to this model, the total current flowing across a Josephson contact consists of the following components:

$$I = I_i \sin \varphi + \frac{V}{R} + C \frac{\mathrm{d}V}{\mathrm{d}t} + I_\mathrm{P}(t). \tag{4.3}$$

The first term in this expression represents the Josephson supercurrent  $(I_j = (2e/\hbar)E_j)$ , the second represents the normal component of the current, and the third the displacement current due to the capacitance C of the contact. The fluctuation current  $I_F(t)$  is determined by the thermal and



FIG. 17. The function  $\lg R_{\Box} = f(T^{-1/2})$  for a granulated film of In. Film thickness 5.4 nm, H = 0 (1) and 43.7 (2) kOe (Ref. 22).

quantum noise. It is assumed that the resistance R in (4.3) is determined either by quasiparticle tunneling or by an ohmic shunt. Since  $d\varphi/dt = (2e/\hbar)V$ , we may rewrite (4.3) in the form of the following equation for the phase:

$$I = \frac{\hbar}{2e} C \frac{d^2 \varphi}{dt^2} + \frac{\hbar}{2e} \frac{1}{R} \frac{d\varphi}{dt} + I_i \sin \varphi + I_F(t).$$
(4.4)

The expression given by (4.4) is the equation for damped oscillations. If we neglect fluctuation and dissipation terms for the zero current (I = 0), and assume small  $\varphi(\sin\varphi \sim \varphi)$ , we obtain the equation for a harmonic oscillator. In general, the phase dynamics within the framework of the resistive model is equivalent to the motion of a fictitious particle in the "washboard potential" of Fig. 18. The height of the barriers of this potential is determined by the Josephson energy  $E_i$  (Refs. 32 and 34) and decreases with increasing current (Fig. 18). The superconducting coherence corresponds to the localization of the phase "particle" in the potential well. If the "particle" has a high enough probability of passing through the barrier, the contact will assume its normal state. When the temperature is high enough, the delocalization of the "particle" will occur by a classical hopping over the barrier. The probability of such hops decreases exponentially with decreasing temperature, and the result is that the resistance of the contact tends to zero and phase coherence is established. At low enough temperature, however, quantum phase fluctuations begin to play a significant part, and the probability of quantum tunneling of the "particle" through the barrier becomes significant.

The resistance model can be extended to a system of coupled Josephson contacts,<sup>34,36,37,40</sup> where, as shown in Ref. 36, this model (in contrast to the above models that take into account only the charging energy  $E_c$ ) is not very sensitive to disorder, i.e., to the statistical spread of  $E_j$ . Attempts to take dissipation into account<sup>34,41</sup> have shown that the role of quantum tunneling increases with increasing resistance R in (4.4), which, for two-dimensional systems, can be identified with the normal resistance  $R_{\Box}$  above  $T_c$ . It was shown in Refs. 33–41 that, in this case, the resistance does not fall to zero for  $R_{\Box} \gtrsim aR_Q$  ( $R_Q = \pi\hbar/2e^2$ , where a is of the order of unity), but remains finite (Sec. 2). Moreover, according to Refs. 40 and 41, the resistance can increase as the temperature is reduced further, and can pass through a minimum. This effect is due to the suppression of Josephson couplings



FIG. 18. Schematic graph of the potential energy E of the Josephson contact as a function of the phase difference  $\varphi$  for I = 0 and  $I \neq 0$ .



FIG. 19. The function  $R_{\Box}(T)$  for a film of amorphous Bi, approximately 1.5 nm thick, <sup>134</sup> for H = 0. Insert shows the "tails" of the resistance curves for the superconducting junction for H = 0 (1) and 47 (2) kOe.

as a result of the enhancement of quantum phase tunneling as the temperature is reduced.

A qualitative confirmation of this for ultrathin amorphous films of bismuth<sup>134,135</sup> has been reported in Refs. 40 and 41. The resistance minimum for  $T < T_{c0}$  was found to appear in these films for  $R_{\Box} \gtrsim Q_{O}$ , and there were instances (Fig. 19) in which the resistance fell by three or four orders of magnitude with decreasing temperature, but remained finite, and then rose again, forming a minimum. Non-ohmic effects were practically absent for samples with  $R_{\Box} \approx R_{Q}$ , and the weak negative temperature variation of resistance for  $T > T_c$  (Fig. 19) was determined by WLE and EEI effects.<sup>3-5</sup> The magnetic field H shifts the R(T) curves toward lower temperatures and leads to an increase in resistance at the minimum. The R(T) curves recorded for H = 0 and  $H \neq 0$ , are then found to cross and, at low temperatures, the magnetoresistance is negative. It has been found<sup>134,135</sup> that, for samples of higher resistance, the reentrant effects depend on the applied voltage V, and the nonmonotonic dependence, including the minimum, is recorded not only for R(T), but also for R(H) and R(I), where I is the current. Existing models of the quasireentrant behavior in the dissipative systems of Josephson contacts<sup>34,40,41</sup> are essentially qualitative [for example, they do not describe the functional form of R(T) near the minimum]. The nonmonotonic behavior of R(I) was predicted in Ref. 41. The common feature of the nonmonotonic dependence of R on T, H, and I, found in Refs. 134 and 135, is that an increase in any of these variables is accompanied by the enhancement of the pairbreaking processes.

As an example of the possible influence of quantum phase fluctuations on reentrant phenomena in films of amorphous bismuth, <sup>134,135</sup> we consider the behavior of the function R(I). It has been found (Fig. 20) that the position of the minimum  $(I_{\min})$  on the R(I) curves at first increases with increasing temperature, and then declines again [for comparison, Fig. 20 also shows the nonmonotonic form of R(T)]. The function  $I_{\min}(T)$  has a relatively sharp maximum for  $T \sim 2.4$  K [whose position on the temperature scale coincides with the minimum of the function R(T)], but is asymmetric and resembles the letter  $\lambda$ . The left-hand (low-



FIG. 20. The functions  $I_{\min}(T)$  (1) and  $R/R_n = f(T)$  (2) for a film of amorphous Bi, approximately 1.2 nm thick ( $R_{\Box} \approx 11 \text{ k}\Omega$ ; Ref. 34). The experimental uncertainties are indicated in the  $I_{\min}(T)$  curve.

temperature) wing of this function is shallower than the right-hand wing and there are reasons to suppose that  $I_{\min}$ tends to a constant as the temperature is reduced. The righthand (high-temperature) wing of  $I_{\min}(T)$  is steeper, and lies in the range of the sharp increase in R with increasing temperature, i.e., in the region of the transition from the superconducting to the normal state. According to Ref. 41,  $I_{\min}$  should decrease with increasing  $E_i$ , i.e., with increasing barrier height for the phase "quasiparticle", under the conditions of quantum phase tunneling. In accordance with (3.15), the energy increases with decreasing temperature, but tends to a constant at sufficiently low temperatures. It is therefore very probable that, in accordance with Ref. 41, the function  $I_{\min}(T)$  mirrors the behavior of  $E_i$ . These qualitative considerations are also found to apply to other features of R(T, V, I, H) or amorphous bismuth films.<sup>134,135</sup> Despite this, further theoretical and experimental studies are necessary to elucidate the role of quantum phase tunneling in quasireentrant phenomena.

Studies of reentrant phenomena in disordered superconductors are rapidly expanding. This means that our presentation of existing experimental data can hardly be regarded as final or the only possible one. In particular, it is essential to have further experimental studies of the threshold resistance  $R_{\Box} \approx R_Q = \pi \hbar/2e^2$  of two-dimensional systems (Ref. 145).

#### **5. CONCLUSION**

The substantial advances in our understanding of the electronic properties of disordered conductors<sup>1-6</sup> achieved in recent years have led to significant successes in the theory of the effect of disorder on superconducting properties. New mechanisms have been proposed for the effect of disorder on  $T_c$  and  $H_{c2}$ , and there is a much improved understanding of the conducting and superconducting properties of granulated metals. Significant results have been obtained as a result of theoretical and experimental studies of reentrant phenomena in heterogeneous systems, due to the competition

between superconductivity and localization of electrons.

At the same time, many aspects of this problem are still not understood. All one can say at present is that we have a more or less satisfactory understanding of only the influence of weak disorder  $(\lambda \leq 1)$ . Very little attention has been devoted to problems involving strong disorder ( $\lambda \leq 1$ ). This applies particularly to  $H_{c2}$  and the fluctuational conductivity near  $T_c$ . The reason for this has been the complexity of the problem in which we have to take into account a great variety of possible effects of disorder on superconducting properties. There are, as yet, no sufficiently universal approaches that could be used in a wide range of disorder to describe the variation in the superconducting properties as the MIT is approached. There is a lack of theories capable of dealing with a wide class of superconducting materials. Existing theories (especially for systems near the MIT) frequently take into account only one of the possible effects of disorder on the superconducting properties, and ignore all others. Real materials do not therefore fit into the Procrustean bed of theoretical models. Moreover, discussions of experimental results frequently suffer from a lack of clear criteria for testing existing mechanisms for the effects of disorder.

The above difficulties in theoretical descriptions and analyses of experimental data are due to the above-mentioned lack of a unified approach to the description of the MIT. Existing approaches take disorder into account to some extent when they evaluate the effect of disorder on different properties of electrons, such as the mean free path, density of states, EEI, EPI, spin properties, Coulomb effects, inelastic relaxation, and so on. Any of these factors may also affect superconductivity, but theoretical and experimental estimates of the relative contribution of each of them in particular systems are still exceedingly difficult.

Still greater complexity is encountered in the study of heterogeneous systems although percolation theory has been fruitful in this field. Considerable theoretical advances have also been made in the case of granulated metals. Studies of artificially prepared (e.g. by electron lithography) regular two-dimensional granulated systems are desirable from the point of view of verification of theoretical models. It should be possible to take into account exactly the influence of different factors in such cases, including charging effects, statistical spreading of tunneling resistances, and so on. This type of system may also be very useful in the study of reentrant phenomena.

Finally, we note that studies of the effect of disorder on the superconducting properties may reveal some new features of the MIT. For example, they may provide the answer to the question: how should we interpret the existence of the characteristic threshold resistance  $R_{\Box} \approx R_Q = \pi \hbar/2e^2$  in two-dimensional systems? Is it exclusively due to quantum phase fluctuations in heterogeneous superconducting systems? Is it consistent with the scaling theory of localization in which there is no minimum metallic conductivity at the MIT (especially for two-dimensional systems)? Further research into these interesting topics should provide the answers to these and many other questions, and lead us to new problems and as yet unknown properties of disordered systems.

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- <sup>1)</sup> The reduction in  $T_c$  with increasing disorder is typical for all superconductors with  $T_c \gtrsim$  7-8 K.
- <sup>2)</sup> We note that, according to Ref. 5, the second term in (3.5) for twodimensional systems can also be treated as a reduction in  $\mu^*$  with increasing disorder.
- <sup>3)</sup> Most of what we shall say about three-dimensional granulated metals is also valid for two-dimensional island films.
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