Measured Width of Superconducting Transition: Quantitative Probe of Macroscopic Inhomogeneities

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The range of upper critical fields, as deduced from the field-dependent width of resistivity curves, reflects the structure of inhomogeneities in a superconductor. Within a Gaussian model of conductivity fluctuations the maximum upper critical field as a function of temperature yields both the magnitude of the conductivity fluctuation $\delta\sigma/\sigma$ and the spatial range l_{inh} of the inhomogeneity. Good fits to the data are achieved from $l_{\text{inh}} \sim \xi(0)$ and $\delta\sigma/\sigma \sim \frac{1}{4}$.

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Spatial inhomogeneities can strongly influence superconducting properties when their characteristic length scales are comparable to the superconducting coherence length. The resulting deviations from the universal behavior of ordinary (weak-coupling) superconductors occur in three classes of materials: in metastable systems such as metallic glasses and alloys where the magnitude of the deviation seems to correlate with the metallurgical treatment,[1] in synthetic structures such as superlattices,[2] and in granular samples and segregation systems which contain well defined superconducting clusters embedded in a dielectric medium or a normal metal.[3]

Theoretical studies have focused on the granular systems where the influence of disorder on superconductivity can be described by percolation models.[4] However, models assuming well separated, weakly coupled superconducting regions cannot be applied to systems where the properties vary smoothly on the atomic scale. This is the case in many metastable systems and probably also in many superlattices as a result of interdiffusion.

This paper (1) describes the results of a microscopic theory of superconductors which includes the effects of slowly varying inhomogeneities and (2) provides a method of analyzing related experiments. The theory exploits the temperature dependence of the coherence length $\xi(T)$. Near T_c the coherence length is very large and the superconducting properties are determined by the averaged properties of the sample. As the temperature is lowered inhomogeneities on the length scale of $\xi(T)$ can be resolved, leading to deviations from averaged properties. The temperature dependence of the observed deviation will reflect the type of inhomogeneity and its length scale.

Figure 1 illustrates both the experimental results and the methods proposed in this paper for understanding them. The actual experiment is to measure the resistivity versus temperature for a set of magnetic fields. The circles denote the field strength at which half the normal-state resistivity has been restored. This field as a function of temperature is routinely cited as the upper critical field $H_{c2}(T)$ for inhomogeneous samples. This H_{c2} is "enhanced" above the expected BCS value (shown as a dashed-dotted line) as the temperature is lowered. This slight enhancement is a feature of the theory presented here.[5]

A more striking feature of the resistivity data is that the magnetic field width of the transition increases with decreasing temperature. The 90% and 0% resistivity points are shown as squares in Fig. 1. Traditionally, this broadening has been ignored by theorists. Fitting our theory to the data (dashed lines in Fig. 1) gives both the magnitude of the conductivity fluctuations and the length scale on which they occur.

The theory leading to the results shown in Fig. 1 is based on the quasiclassical method and will be discussed in a longer paper. The idea of the calculations can be discussed more simply. First we must generalize the pair-breaking parameter ρ to an inhomogeneous system. For a dirty but homogeneous system the upper critical field $H_{c2}(T)$ separating the normal and superconducting phases is given in terms of the digamma function $\psi(z)$ by

$$\ln\left(\frac{T}{T_c}\right)+\psi\left(\frac{1}{2}+\frac{\rho^0(H)}{2\pi k_B T}\right)-\psi\left(\tfrac{1}{2}\right)=0, \qquad (1)$$

where the homogeneous pair-breaking parameter is

$$\rho^0(H)=\left(\frac{\sigma_0}{3\gamma_0}\,\frac{k_B^2 h}{e^2}\right)\frac{2\pi}{\phi_0}H = \frac{4}{\pi}\,\frac{H}{(-dH_{c2}/dk_B T)_{T=T_c}}. \qquad (2)$$

Equation (1) produces the dash-dotted curve in Figs. 1 and 3; the actual value of the zero-tem-

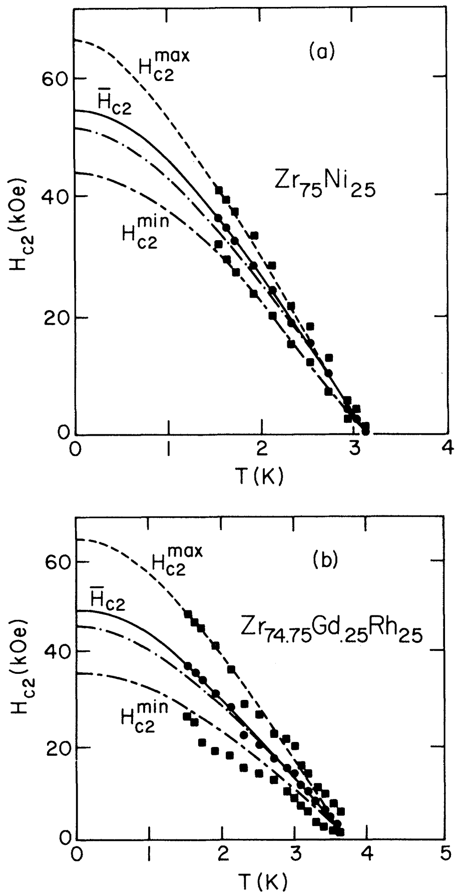

FIG. 1. Comparison of data (Ref. 1b) with theory for magnetic-field dependence of the resistivity transition as a function of temperature. The experimental data (theoretical results) are denoted by squares (short-dashed line, $H_{c2}^{\max}$; and long-dash–short-dashed line, $H_{c2}^{\min}$) for the 90% and 0% points on the resistivity curve and by circles (solid line, $\bar{H}_{c2}$) for the midpoints. In addition, the BSC upper critical field $H_{c2}(T)$, based on its slope at the critical temperature, is shown as a dash-dotted line. (a) For the $Zr_{75}Ni_{25}$ sample, $H_{c2}(0)=41$ kG [i.e., $\xi(0)=90$ Å], $\delta\sigma/\sigma_0=0.3$, and $l_{\rm inh}/\xi(0)=0.5$ produce the theoretical curves shown. (b) For $Zr_{74.75}Gd_{0.25}Rh_{25}$, the equivalent numbers are $H_{c2}(0)=53$ kG, $\delta\sigma/\sigma_0=0.2$, and $l_{\rm inh}/\xi(0)=2.0$. A small constant pair-breaking parameter ($\Delta\rho=0.55$ K) has been included to account for the T_c depression due to paramagnetic scattering from the Gd impurities. The deduced inhomogeneity parameters are insensitive to variation of the small additional pair-breaking parameter.

perature upper critical field $H_{c2}(0)=0.693T_c \times(-dH_{c2}/dT)_{T_c}$ depends on the averaged conductivity σ_0 and the averaged electronic specific-heat coefficient γ_0.

In an *inhomogeneous* system the conductivity (and specific heat) fluctuates. For simplicity we model

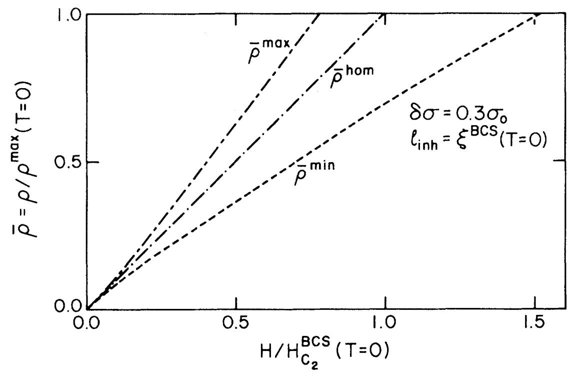

FIG. 2. Broadening of the pair-breaking parameter spectrum due to inhomogeneities. The increasing splitting of the band edges of $A(\rho,H)$, $\bar{\rho}^{\max}$ and $\bar{\rho}^{\min}$, as a function of the external magnetic field reflects the increasing spatial resolution of inhomogeneities.

the fluctuations of only the conductivity by a magnitude $\delta\sigma$ and an inhomogeneity length scale $l_{\rm inh}$ according to the distribution

$$\langle\delta\sigma(\vec{R})\,\delta\sigma(\vec{R}')\rangle_{\rm av} =\frac{(\delta\sigma)^2}{(l_{\rm inh}\sqrt{2\pi})^3}\exp\left[-\frac{1}{2}\frac{(\vec{R}-\vec{R}')^2}{l_{\rm inh}^2}\right]. \quad (3)$$

These fluctuations give rise to fluctuations in the pair-breaking parameter ρ which can be characterized by a spectral weight function $A(\rho,H)$ with the following properties, illustrated in Fig. 2: (i) $A(\rho, H)$ is nonzero only for $\bar{\rho}_{\min}(H)<\rho<\bar{\rho}_{\max}(H)$. These $\bar{\rho}_{\min}(H)$ and $\bar{\rho}_{\max}(H)$ then, via (1), give the lower and upper dashed lines in Fig. 1 and in Fig. 3 for the parameters of Fig. 2. (ii) The solid line in Figs. 1 and 3, given by

$$\bar{H}_{c2}(T)=\int dH\,HA(\rho,H)/\int dH\,A(\rho,H), \quad (4)$$

is the upper critical field associated with the midpoint of the resistive transition. The enhancement of $\bar{H}_{c2}$ with respect to the homogeneous result (dash-dotted curves in Figs. 1 and 3) can be understood from the facts that H_{c2} is proportional to $1/\sigma$ and that $\langle 1/\sigma\rangle > 1/\langle\sigma\rangle$.

To discuss the calculation of the spectral $A(\rho, H)$, we start with the linear equation for the existence of a superconductivity gap function:[6]

$$\Delta(\vec{R})=\int d^3R'\{\int_0^\infty dt\,K(\vec{R},\vec{R}',t)\}\Delta(\vec{R}'), \quad (5)$$

with

$$K(\vec{R},\vec{R}',t)=2\pi\lambda\sum_n\exp(-2|\epsilon_n|t)g(\vec{R},\vec{R}';t).$$

Here $\epsilon_n=(2n+1)\pi k_{\rm B}T$ are the Matsubara frequencies and the correlation function

$$g(\vec{R},\vec{R}',t) = -\int_{-\infty}^{\infty}\frac{d\omega}{\pi}e^{-i\omega t}\int_{-\infty}^{\infty}\frac{d\Omega}{2\pi}\,\mathrm{sgn}(\Omega+\omega)\,\mathrm{sgn}(\Omega-\omega)$$
$$\times\langle[G(\vec{R},\vec{R}',\Omega+\omega)-G^*(\vec{R}',\vec{R},\Omega+\omega)][G(\vec{R},\vec{R}',\Omega-\omega)-G^*(\vec{R}',\vec{R},\Omega-\omega)]\rangle \quad (6)$$

is given in terms of products of normal-state Green's functions averaged over the impurities.[7]

In a homogeneous dirty system this function decays exponentially as $e^{-2\rho t}$, where ρ is the pair-breaking parameter. For an inhomogeneous system there will be a range of pair-breaking parameters whose distribution is described by the spectral weight function

$$A(\vec{R},\vec{R}',\rho H) = L^{-1}\{g(t)\} = \mathrm{Im}\tilde{K}(\vec{R},\vec{R}',\rho)/\pi, \quad (7)$$

where $L^{-1}\{g\}$ denotes the inverse Laplace transform of $g(\vec{R},\vec{R}',t)$.

The derived[8] equation of motion of $\tilde{K}(\vec{R},\vec{R}',\rho)$ can be understood by analogy with the diffusion equation $\dot{n} = -\nabla\cdot\vec{J} = \nabla\cdot[D(\vec{R})\nabla n]$. The appropriate differential operator here is

$$P^{\mathrm{op}}\{\sigma(\vec{R})\} = -\frac{1}{2}\frac{1}{3}\frac{\sigma_0}{\gamma_0}\frac{k_B^2 h}{e^2}\bar{\partial}\frac{\sigma(\vec{R})}{\sigma_0}\bar{\partial}, \quad (8)$$

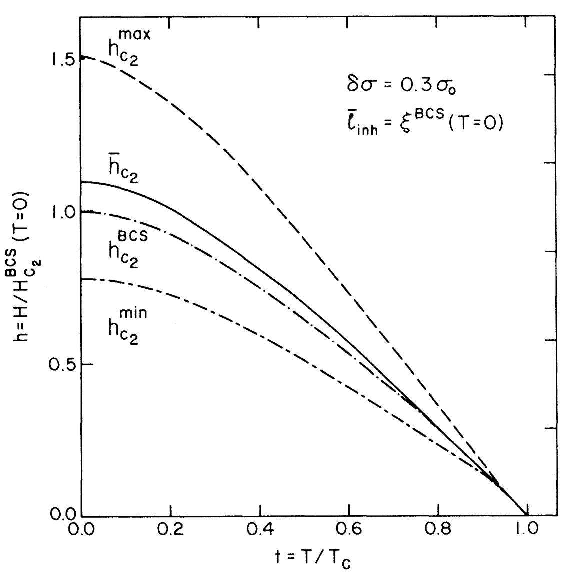

FIG. 3. Critical fields characterizing the resistive transition of an inhomogeneous superconductor in a magnetic field. $\bar{h}_{c2}$ is the (reduced) critical field determined from the averaged kernel, and $h_{c2}^{\max}$ and $h_{c2}^{\min}$ are the critical fields related to the band edges $\bar{\rho}^{\min}$ and $\bar{\rho}^{\max}$, respectively, of $A(\rho,H)$.

where $\bar{\partial} = \nabla + i(2\pi/\phi_0)\vec{A}$. We use the gauge choice $A_y = Hx$, $A_x = A_z = 0$. [Note that $\sigma(\vec{R})k_B^2/3\gamma_0 e^2 = D(\vec{R})/\pi^2$.] Then the equation of motion $(\rho - P^{\mathrm{op}})\tilde{K}(\vec{R},\vec{R}',\rho) = \delta(\vec{R}-\vec{R}')$ has a formal solution for $\tilde{K}$ averaged with respect to the distribution of conductivity fluctuations (3):

$$\langle\tilde{K}(\vec{R},\vec{R}',\rho)\rangle_{\mathrm{av}} = \langle[\rho - P^{\mathrm{op}}\{\sigma_0 + \delta\sigma(\vec{R})\}]^{-1}\rangle_{\mathrm{av}} = [\rho - P\{\sigma^0\} - \Sigma]^{-1}. \quad (9)$$

The self-energy Σ is given by

$$\Sigma = \langle(P^{\mathrm{op}}\{\delta\sigma\})^2\rangle_{\mathrm{av}}/(\rho - P^{\mathrm{op}}\{\sigma^0\} - \Sigma). \quad (10)$$

This simple form for the self-energy can be calculated in terms of eigenfunctions of $P^{\mathrm{op}}\{\sigma_0\}$. In particular

$$\langle(P^{\mathrm{op}}\{\delta\sigma\})^2\rangle_{\mathrm{av}} = \left\{\rho^0(H)\frac{\delta\sigma}{\sigma_0}\right\}^2\frac{h(1+h^2)}{(1+h)^3}, \quad (11)$$

where $h = [l_{\mathrm{inh}}/\xi(0)]^2 H/H_{c2}(0)$ is the effective magnetic field in units of $\phi_0/2\pi l_{\mathrm{inh}}^2$. The low-field behavior ($\propto H^3$) can be qualitatively understood as follows: The matrix element of P^{op} is proportional to H [cf., Eq. (2)], the extra factor of H coming from the degeneracy of the Landau level.

The averaged spectral function $A(\rho,H)$ giving the "density of states" for the pair-breaking parameters and hence, via (1), the distribution of H_{c2} for the inhomogeneous system, is now easily calculated. In the limit of large magnetic fields, it simplifies to

$$A(\rho,H) \propto \mathrm{Im}\left[\left(\frac{H_{\min}(\rho)}{H} - 1\right)\left(\frac{H_{\max}(\rho)}{H} - 1\right)\right]^{1/2}. \quad (12)$$

Here $H_{\max(\min)}(\rho)$ are related to the $\rho_{\min(\max)}$ shown in Fig. 2. In particular

$$\rho_{\min(\max)} = \rho^0(H) \mp 2\langle(P^{\mathrm{op}}\{\delta\sigma\})^2\rangle_{\mathrm{av}}^{1/2}. \quad (13)$$

Then $H_{\max}(\rho)$ and $H_{\min}(\rho)$ correspond to the intersection of the $\rho_{\min}(H)$ and $\rho_{\max}(H)$ curves, respectively, for a given ρ. The resulting $H_{\max(\min)}$ as a function of temperature, plotted in Fig. 3 as $h_{c2}^{\max(\min)}$, are deduced from Eq. (1) with $\rho^0(H)$

replaced by $\rho_{\min(\max)}$. In addition, the value of the midpoint $\bar{H}_{c2}$ is given by $\frac{1}{2}(\sqrt{H_{\max}}+\sqrt{H_{\min}})^2$.

Finally we turn to how the two parameters in the model, $\delta\sigma$ and $l_{\rm inh}$, are determined from the data. In the limit of large $H_{c2}(T)$, $H_{c2}^{\max}(T)/H_{c2}^{\rm BCS}(T)=1+2\,\delta\sigma/\sigma_0$. As $H_{c2}(T)$ decreases, the asymptotic form is

$$1-\frac{H_{c2}^{\rm BCS}(T)}{H_{c2}^{\max}(T)}\simeq 2\frac{\delta\sigma}{\sigma_0}\left[1-\frac{3}{2}\left(\frac{\xi(0)}{l_{\rm inh}}\right)^2\frac{H_{c2(0)}}{H_{c2}^{\max}(T)}\right]. \tag{14}$$

Plots according to (14) were used to deduce the parameters for the systems shown in Fig. 1: $Zr_{75}Ni_{25}$, $\delta\sigma/\sigma_0=0.3$ and $l_{\rm inh}/\xi(0)=0.5$; $Zr_{74.75}Gd_{0.25}Rh_{25}$, $\delta\sigma/\sigma_0=0.2$ and $l_{\rm inh}/\xi(0)=2.0$.

This is the first theory for inhomogeneous superconductors, demonstrating that the inhomogeneity scales can be deduced from measurements of H_{c2} or rather from the resistivity widths, data which in the past have been largely ignored. The theory does not depend on there being small changes in the parameters but only that the changes are gradual on the atomic scale, i.e., $k_F l_{\rm inh} >> 1$.

There is some evidence for inhomogeneity scales of order 50–100 Å, but not much on the form of that inhomogeneity. For example, small-angle x-ray scattering[9] on $(Mo_{0.6}Ru_{0.4})_{82}B_{18}$, which exhibits an enhanced H_{c2} at low temperature,[10] reveals an inhomogeneity scale of order 50 Å. The only evidence as to its nature comes from a microprobe study[11] of a similar (but not superconducting) material $Fe_{40}Ni_{40}B_{20}$ for which boron-rich domains were observed. Another example is in the superconducting amorphous alloy $Zr_{100-x}Si_x$ where fluxoid pinning, believed to be most strongly influenced by inhomogeneities of order $\xi(0)$, was correlated with the enhancement of H_{c2}.[12] The present theory would yield similar results from inhomogeneities due to microcrystallization, phase separation, fluctuations in atomic concentration, or anything that produced variations in the conductivity on ~100 Å scale.

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[6]See, for example, D. Saint-James, G. Sarma, and E. J. Thomas, *Type II Superconductivity*, Monographs in Natural Philosophy, Vol. 17 (Pergamon, Oxford, 1969) Sec. 5.4.

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