Superconducting Metals in Porous Glass as Granular Superconductors

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The critical fields of superconductors in porous glass are found to have the same temperature dependence as the critical field of a homogeneous dirty alloy. An effective mean free path for electrons in the normal state can be deduced; it is proportional to the pore diameter but is much smaller. This is most easily explained if the superconductor consists of grains separated by tunneling barriers, for this gives a mean free path equal to the grain size multiplied by an average of the transmission coefficient of the barriers. This model can also give a plausible explanation of the large change in critical field produced by chemical treatment of the glass before impregnation with metal. Parmenter's theory of granular superconductors shows that vortices can exist in such materials, and the critical current should be determined by vortex pinning. The measured critical current for indium in porous glass is less than that calculated from a Parmenter formula which assumes that the fields in the sample are uniform.

CRITICAL FIELD

A GRANULAR superconductor is one consisting of small grains which are separated spatially but connected by electron tunneling. An explanation of the critical-field behavior of superconducting indium, lead, and other metals in porous glass is provided in the granular superconductor theories of Abeles *et al.*[1] and Parmenter.[2]

The preparation of porous glass and the subsequent preparation of samples containing metal have been described in the literature.[3,4] The pore diameters (d) were measured by mercury porosimetry,[5] and the values obtained were in agreement with those obtained from electron microscope pictures of the structure.[6] The form of the metal in porous glass may be described as beads of approximately equal size touching one another.[6]

The temperature dependence of the critical field of metals in porous glass is described by the function[4]

$$h(t)=U(t)\,, \tag{1}$$

where t is the reduced temperature T/T_c, $h(t)$ is the reduced field $H_{c2}(T)/H_{c2}(0)$, and the function $U(t)$ is defined by

$$\ln(1/t)=-\psi(\tfrac{1}{2})+\psi(\tfrac{1}{2}+U/4\gamma t)\,. \tag{2}$$

Here $\psi(x)$ is the logarithmic derivative of the γ function and $\gamma=e^C=1.781$, C being Euler's constant. The function U will be called the "universal function." It differs from the function defined by de Gennes[7] by a factor $\pi/\gamma=1.76$; the definition above has the property $U(0)=1$.

Measured values of the critical field of indium, lead, tin, and thallium are shown in Fig. 1. The quantity plotted is $H_{c2}\xi_0 d/\Phi_0 U(t)$, where Φ_0 is the flux quantum, and $\xi_0=hv_f/1.76\pi kT_c$ is the coherence length of the pure metal. The critical field corresponds to the onset of superconductivity, as determined by the mutual inductance method. The value of the critical field H_{c2} does not depend on the amplitude of the ac field for fields up to 16 Oe. The ac field used was 1 Oe. The figure shows that Eq. (1) holds for reduced temperatures up to about 0.8 for most samples, but there are some unexplained deviations for larger t. It will also be noted that H_{c2} is inversely proportional to d, as reported earlier for indium.[4]

This behavior of the critical field as a function of t and d is in agreement with the de Gennes[7,8] and Maki[9] theories of homogeneous dirty superconductors, if it is assumed that the electronic mean free path in the normal state l is proportional to d. This would be expected if l were determined by boundary scattering.

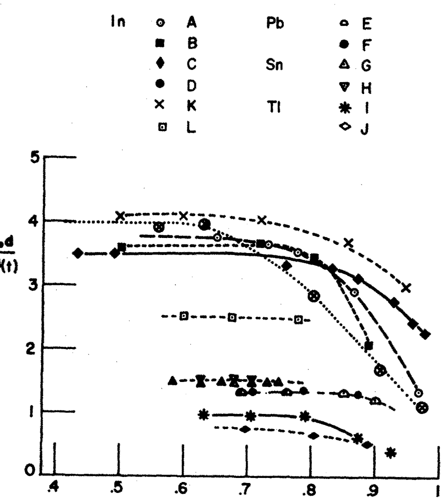

FIG. 1. The critical field of superconductors in porous glass as a function of temperature and pore diameter.

[1] B. Abeles, Roger W. Cohen, and W. R. Stowell, Phys. Rev. Letters **18**, 902 (1967).
[2] R. H. Parmenter, Phys. Rev. **154**, 353 (1967); **167**, 387 (1968).
[3] C. P. Bean, Rev. Mod. Phys. **36**, 31 (1964).
[4] J. H. P. Watson, Phys. Rev. **148**, 223 (1966).
[5] L. C. Drake, Ind. Eng. Chem. **41**, 780 (1949).
[6] R. J. Charles, J. Am. Ceram. Soc. **47**, 154 (1964).
[7] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966).
[8] P. G. de Gennes, Physik Kondensierten Materie **3**, 79 (1964).
[9] K. Maki, Physics **1**, 21 (1964).

TABLE I. Critical field and temperature, and derived properties in untreated porous glass.

Indium	d(Å)	$T_c(K)$	$H_{c2}(0)$ (kOe)	ξ_0(10^5 cm)[a]	τ	l(Å)
A	31	4.240	69	3.5	0.042	1.31
B	53	4.170	40	3.59	0.041	2.19
K	60	4.050	39	3.70	0.036	2.17
C	71	3.956	29	3.75	0.041	2.94
D	80	3.960	29	3.75	0.036	2.90
Lead						
E	32	7.049	96	0.85	0.120	3.84
F	58	7.150	55	0.83	0.120	6.90
Tin						
G	31	4.936	54	1.72	0.11	3.42
H	39	4.248	39	2.0	0.104	4.40
Thallium						
I	32	2.649	48	1.17	0.175	5.59
J	58	2.612	21	1.19	0.216	12.5

[a] The coherence length ξ_0 is the pure bulk metal, corrected for the change in T_c, taking $\xi_0 \propto T_c^{-1}$.

However, according to the de Gennes–Maki theories,

$$H_{c2}(0)=(3/2\pi^2)(\Phi_0/\xi_0 l). \tag{3}$$

If Eq. (3) is used to determine l, l is smaller than d by an order of magnitude shown in Table I. Thus, for indium in untreated porous glass, $l/d \simeq 0.04$. A ratio close to unity would be expected for boundary scattering. On the other hand, if the very short mean free path is attributed to disorder in the grains, it is difficult to see why l is proportional to d.

Abeles *et al.*[1] have carried out a calculation for a one-dimensional model of a granular superconductor, with the grain boundaries represented by δ-function barriers. They found the material behaves like a homogeneous dirty superconductor, with a critical field given by Eqs. (1) and (3) near T_c, but with an effective mean free path

$$l=a\tau/(1-\tau), \tag{4}$$

where a is the grain size and τ is the transmission coefficient for electrons incident on a δ-function barrier. A simple calculation gives a result very similar to Eq. (4) for the effective mean free path in three dimensions, provided the transmission coefficient is small.

The starting point is Harrison's equation[10] for the tunneling current density in the normal state in the WKB approximation,

$$J=\frac{e}{4\pi^3\hbar}\int_{-\infty}^{\infty} dE[f(E)-f(E+eV)]\int_E dS\, e^{-\eta}, \tag{5}$$

where V is the voltage across the barrier, $\int dS$ is an integral over the projection of the constant-energy surface of energy E onto the plane of the barrier, i.e., an integral over the momentum component in the plane of the barrier, and $e^{-\eta}$ is the transmission coefficient in the WKB approximation.[11] For degenerate Fermi statistics and small applied voltages, Eq. (5) becomes

$$J=\frac{e^2V}{4\pi^3\hbar}\int_{E_F} dS\, e^{-\eta}.$$

But, almost the whole voltage drop is across the junctions, so the average electric field $E=V/a$, where a is the grain size. The conductivity is, therefore,

$$\sigma=\frac{e^2a}{4\pi^3\hbar}\int_{E_F} dS\, e^{-\eta}. \tag{6}$$

But, for a normal metal with mean free path l,[12]

$$\sigma=e^2lS_F/12\pi^3\hbar, \tag{7}$$

where S_F is the area of the Fermi surface, comparing Eqs. (6) and (7),

$$\frac{l}{a}=\frac{3}{S_F}\int dS\, e^{-\eta}. \tag{8}$$

The right-hand side of Eq. (8) is essentially an average of the transmission coefficient over the angle of incidence of the electron on the barrier. If this same argument is used in one dimension, the result is

$$l/a=\tfrac{1}{2}\exp[-\eta(E_F)], \tag{9}$$

which agrees with Eq. (4) for small τ if $\tau=\frac{1}{2}e^{-\eta}$.

Thus, the assumption that the system is granular provides an explanation for the fact that the critical field is inversely proportional to d, but with an effective mean free path from Eq. (3) much less than d, provided we make the reasonable assumption that the grain size a is about equal to d. The values of the effective transmission coefficient τ, defined as l/d, are shown in Table I. There does not appear to be a dependence of τ on d. For indium in untreated porous glass, τ ranges between 0.037 and 0.043. The values for lead and tin are about 0.1, and for thallium about 0.2, indicating that the grains are more strongly coupled than for indium.

The values of τ must depend on the details of the contact between the beads of metal. The shape of the beads and the contact between them must be controlled to a large degree by the energy of the metal-glass interface. Therefore, if the chemical nature of the glass surface were changed prior to impregnation with metal, a different value of τ might be expected. The inside surfaces of normally prepared porous glass are covered with OH groups.[13] These can be removed and replaced with Cl or CH_3O groups. The treatment produces little change in the pore diameter d or in the transition

[10] W. A. Harrison, Phys. Rev. **123**, 85 (1961).

[11] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., Oxford, England, 1965), 2nd ed., p. 173.

[12] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), p. 262.

[13] J. H. P. Watson, Phys. Letters **25A**, 326 (1967).

TABLE II. Critical field and temperature, and derived properties of metals in chemically treated porous glass.

	d(Å)	$T_c(K)$	$H_{c2}(0)$ (kOe)	ξ_0(10^5 cm)	τ	l(Å)
Chlorinated glass						
L	60	4.000	24	3.7	0.059	3.54
M	60	4.010	24	3.7	0.059	3.54
Methylated glass						
N	60	4.050	37	3.7	0.038	2.30

temperature, but the critical fields are decreased. This can be interpreted as an increased transmissivity τ, as shown in Table II. The values of τ are increased by a factor of about 1.5 for the chlorinated glass, but methylation has little effect. This effect would be hard to explain in terms of a decrease in boundary scattering, but can be readily explained in the granular model by a small change in the tunneling barriers.

It is necessary to discuss the temperature dependence of the critical field of a granular superconductor. Parmenter[2] has derived a linearized Ginzburg-Landau equation for such a system, with a coherence length which will be called $\xi_{\mathrm{GL}}(T)$. The critical field H_{c2} is given by

$$H_{c2}(T)=\Phi_0/2\pi[\xi_{\mathrm{GL}}(T)]^2. \tag{10}$$

For T close to T_c, Parmenter's equation for $\xi_{\mathrm{GL}}(T)$ gives a result in agreement with Eqs. (1) and (3), derived from the depairing theory.[7] But at $T=0$, the use of Eq. (10) with Parmenter's equation would give

$$H_{c2}(0)=\frac{6}{\pi^3}\frac{\Phi_0}{\xi_0 l}\frac{1}{N(0)V}, \tag{11}$$

where $N(0)V$ is the BCS interaction parameter.[14] This gives a critical field at $T=0$ greater than Eq. (3) by a factor of about 4 for typical values of $N(0)V$. However, Parmenter's theory is only valid at small magnetic fields. At high fields, it is necessary to take into account the fact that in a magnetic field, part of the Hamiltonian changes sign under time reversal. De Gennes shows[7] that in these circumstances the critical temperature in the presence of the magnetic field is related to the normal-state transport properties. These are completely summarized in the granular system by the mean free path $l=d\tau$. Consequently, the critical field should be determined by the same formulas used for a homogeneous dirty alloy, and, in particular, the temperature dependence should be given by Eq. (1).

Parmenter[2] points out that this can be true only for fields less than the critical field of a single grain. But this is no limitation in practice. The critical field of a single spherical grain of radius R has been given by de Gennes and Tinkham[15]; their result at $T=0$ can be written in the form

$$H_g(0)=(15/2\pi^3)^{1/2}\Phi_0/R(\xi_0 l)^{1/2}. \tag{12}$$

Comparing this with Eq. (3) and identifying R with $\frac{1}{2}d$, we find that $H_g(0)$ is greater than $H_{c2}(0)$, provided $d\lesssim 6.5(\xi_0 l)^{1/2}$. This argument assumes that the same l is as appropriate in Eq. (12) as in Eq. (3). It is not clear whether this is correct, but putting $l\sim R$ in Eq. (12) still leaves the inequality satisfied. The situation at finite temperatures is even better than at $T=0$, because $H_g(t)$ is proportional to $[U(t)]^{1/2}$. A condition of the form $d^2\ll\xi_0 l$ is probably needed to justify Parmenter's continuum assumption.[2]

CRITICAL CURRENT AND OTHER PROPERTIES

Parmenter[2] has derived equations of the Ginzburg-Landau type for a granular superconductor,

$$\xi^2\left(\nabla-i\frac{2e}{\hbar c}\mathbf{A}\right)^2\Delta+\left[1-\frac{g(|\Delta|)}{|\Delta|}\right]\Delta=0, \tag{13}$$

$$\mathbf{J}=\frac{1}{V}\xi^2\frac{(4e)}{\hbar}|\Delta|^2\left[\nabla\varphi-\frac{2e}{\hbar c}\mathbf{A}\right]=0. \tag{14}$$

Here $\Delta=|\Delta|e^{i\varphi}$ is the order parameter, $\mathbf{A}$ is the vector potential, ξ is an effective coherence length (not equal to ξ_{GL} except at $T=0$), and $g(|\Delta|)$ is defined by a certain integral equation. At finite temperatures, g is proportional to $|\Delta|$ for small $|\Delta|$,

$$|\Delta|=g[1+N(0)V\ln(1/t)],$$

so the linearization of Eq. (13) gives

$$\xi_{\mathrm{GL}}^2[\nabla-i(2e/\hbar c)\mathbf{A}]^2\Delta+\Delta=0, \tag{15}$$

with

$$\xi_{\mathrm{GL}}^2=\xi^2\{1+[N(0)V\ln(1/t)]^{-1}\}. \tag{16}$$

At $t=0$, $\xi_{\mathrm{GL}}=\xi$, but ξ is nearly independent of temperature. At no temperature can $g(|\Delta|)$ be expanded in a power series in $|\Delta|$.

In situations were $|\Delta|$ is constant, Eq. (14) gives a London equation with a penetration depth given by[2]

$$\lambda=\lambda_0(\xi_0/l)^{1/2}F_2(t), \tag{17}$$

where λ_0 is the London penetration depth for the pure bulk superconductor, and $F_2(t)$ increases from 1 at $t=0$ to 0.615 $(1-t)^{-1/2}$ at $t\to 1$.

For a thin film of thickness $\ll\xi$ or λ, both $|\Delta|$ and $\mathbf{A}$ can be considered constant, and Eqs. (13) and (14) give a relation between $\mathbf{J}$ and $|\Delta|$. This gives a critical current[2] at $T=0$

$$J_{\mathrm{crit}}=(4e\xi/hV)\Delta_0^2C, \tag{18}$$

where C is a function of $N(0)V$, typically about 0.2. Another limit on the currents in a granular superconductor would seem to be the critical currents J_m of the individual Josephson junctions. Wallace and Stavn[16] have given a formula for J_m, which, in terms of Par-

[14] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[15] P. G. de Gennes and M. Tinkham, Physics **1**, 107 (1964).

[16] P. R. Wallace and M. J. Starn, Can. J. Phys. **43**, 411 (1965).

menter's parameter ξ, is

$$J_m = (8e\xi^2/haV)\Delta_0^2, \tag{19}$$

so $J_{\rm crit}/J_m \sim a/\xi$, which is much smaller than 1.

The observed critical currents are actually less than $J_{\rm crit}$. Values of J_c have been determined experimentally[17] for indium samples with a pore size of about 80 Å; the result extrapolated to $T=0$ is $(8\pm2)\times10^4$ A/cm^2. This discrepancy is not surprising. The dimensions of the samples were much larger than λ or ξ, and the currents and fields were not uniform. The theory of vortices in type-II superconductors depends mainly on the London equations.[7] The nonlinear term in the Ginzburg-Landau equation affects only the structure of the core. Parmenter's theory, therefore, predicts that vortices exist in granular superconductors. If $\kappa=\lambda/\xi\gg1$, the differences between Parmenter's equation and the Ginzburg-Landau equations will cause only a small change in the line energy of a vortex and, perhaps, a change in the vortex lattice for fields near H_{c2} where the cores overlap. The condition $\kappa\gg1$ is very well satisfied in our materials; if it is calculated as $H_{c2}/\sqrt{2}H_c$, we find $\kappa=5490/d$ for indium and $2800/d$ for lead, where d is in Å. If vortices exist, we expect the critical current to be determined by the pinning of these vortices. In granular superconductors, regions where the transmission coefficient τ is smaller than average may occur; such regions might make effective pins because κ is inversely proportional to τ and a larger κ would decrease the line energy of a vortex.

[17] J. H. P. Watson, J. Appl. Phys. 39, 3406 (1968).

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Flux Penetration in an Anisotropic Type-II Superconductor*

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Calculations are presented for the magnetic induction B and the free energy of an anisotropic type-II superconductor near its upper critical field H_{c2}. It is shown that this field is not necessarily parallel to the externally applied magnetic field **H**, its direction depending on the direction of **H** relative to the principal axes of the Ginsburg effective-mass tensor. These results suggest that torque measurements, made on geometrically symmetrical samples, should be useful in determining the upper critical field H_{c2} as well as the components of the effective-mass tensor.

I. INTRODUCTION

According to Ginzburg,[1] the free energy per unit volume F_s of an anisotropic superconductor near to its critical temperature T_c should take the form

$$F_s=F_n+\alpha|\psi|^2+\tfrac{1}{2}\beta|\psi|^4+\sum_{ij}\frac{1}{2m_{ij}}(\phi_i\psi)(\phi_j{}^*\psi^*)+\frac{h^2}{8\pi}, \tag{1}$$

where ψ is the order parameter for the superconducting state, ϕ_i is the ith component of the vector operator $-i\hbar\nabla-(e^*/c)\mathbf{A}$, $\mathbf{h}$ is the microscopic magnetic field, e^* is the effective charge on the superconducting electrons, and α and β are the usual temperature-dependent Ginsburg constants.

Equation (1) differs from the usual Ginzburg-Landau (GL) equation for the free energy in having a mass tensor m_{ij} in place of an isotropic mass. Gor'kov and Melik-Barkhudarov[2] have derived the GL equations for an anisotropic superconductor from the microscopic theory of superconductivity.[3–5] They find that a free-energy expression of the form of Eq. (1) is valid in the region of temperature near T_c in which the penetration depth is much larger than the coherence length. The effective charge e^* is twice the electronic charge e. The mass tensor they obtain is given by

$$\frac{1}{m_{ij}}=\frac{3}{2\epsilon_F}\int v_iv_j\phi(\mathbf{P})N\,ds\Big/\int N\,ds, \tag{2}$$

where ϵ_F is the Fermi energy, v_i is the ith component of the Fermi velocity, and N is the density of states (excluding spin degeneracy) per unit surface area per unit energy range. The integral is over the Fermi surface. The function $\phi(\mathbf{P})$ describes the anisotropy of the energy gap.

The condition for the free energy to be minimum with respect to variations of the order parameter and magnetic field distribution yields the two GL equations.

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[1] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. 23, 236 (1952).

[2] L. P. Gor'kov and T. K. Melik-Barkhudarov, Zh. Eksperim. i Teor. Fiz. 45, 1493 (1963) [English transl.: Soviet Phys.—JETP 18, 1031 (1964)].

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[4] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 36, 1918 (1959) [English transl.: Soviet Phys.—JETP 9, 1364 (1959)].

[5] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 34, 735 (1958) [English transl.: Soviet Phys.—JETP 7, 505 (1958)].