CRITICAL MAGNETIC FIELDS OF GRANULAR SUPERCONDUCTORS

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The superconducting transition temperature T_c of some metals prepared in the form of very thin films[1] or small grains[2,3] is appreciably higher than that of the bulk. A theory of granular superconductors, assuming weak coupling between grains, has been considered by Parmenter.[4] The author obtained an expression for the effective coherence length at absolute zero similar to that for a dirty type-II superconductor.[5] Furthermore, it was suggested[6] that Josephson tunneling between adjacent grains may enhance T_c. In that case one would expect the magnitude of the enhancement to depend strongly on the value of the tunneling matrix element. To shed more light on the phenomenon of the enhancement of T_c, we have investigated the perpendicular critical magnetic fields $H_\perp$ of superconducting Al, Sn, and Ga films consisting of very small grains. The extremely small grain size (~40 Å) gives rise to perpendicular critical fields up to two orders of magnitude larger than the thermodynamic critical fields. Our experimental results indicate that the grains are strongly coupled to each other, and that the enhancement in T_c is independent of the coupling over a wide range of coupling strength. We present an alternative calculation of the critical field, in which no upper limit is placed on the coupling strength between grains. The theory explains the experimental values of $H_\perp$ in a quantitative manner.

Detailed experimental results are presented for aluminum films. The films were evaporated in an oxygen atmosphere from an aluminum-wetted tungsten filament onto a glass substrate at room temperature. The rate of evaporation was about 100 Å/sec, and the oxygen pressure was in the range $(0.5 \text{ to } 1)\times 10^{-4}$ mm Hg. The films were 1 mm wide, and their thickness ranged between 300 and 800 Å. Electron microscopy revealed that the films consisted of grains whose average size was approximately 40 Å. The normal resistivities of the films decreased by less than 10% upon cooling from room temperature to T_c. The critical fields were determined from measurements of dc resistance as a function of magnetic field. The current level was sufficiently low that the resistive transitions were independent of current. The critical field was defined as that field for which the resistance attained one-half its normal-state value. The width of the transitions was approximately 30% of the critical field.

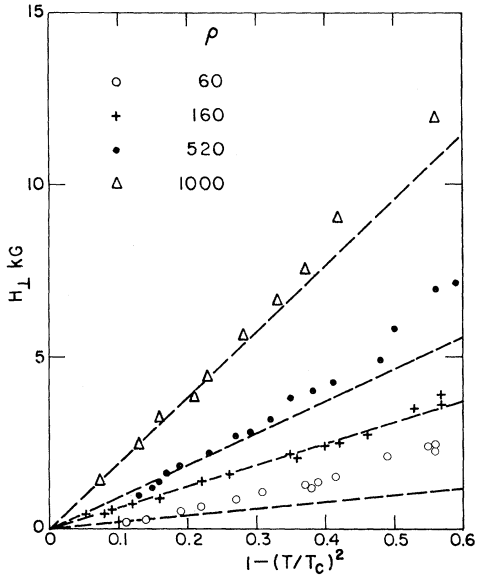

FIG. 1. The critical field $H_\perp(T)$ as a function of $[1-(T/T_c)^2]$ for the four measured samples. The normal resistivities in $\mu\Omega$ cm are indicated in the figure.

In Fig. 1 are plotted the critical fields $H_\perp(T)$ as a function of $[1-(T/T_c)^2]$ for four measured samples. Over an appreciable temperature range, $H_\perp(T) \propto [1-(T/T_c)^2]$. The transition temperatures T_c, normal resistivities ρ_n at T_c, and the values of the slope $dH_\perp/dT$ near T_c for these films are given in the first three columns of Table I.

The extremely large resistivities and the negative temperature coefficient of resistance of the films suggest that the conduction mechanism is tunneling between aluminum grains. The tunneling barriers may be composed of monolayers of aluminum oxide. In order to calculate the critical field near T_c of a system of small superconducting grains separated by tunneling barriers, we first determine the normal-state single-particle Green's function G_n.

Table I. Properties of aluminum films.

T_c (°K)	ρ_n ($\mu\Omega$ cm)	$-dH_\perp/dT\|_{T_c}$ (kG/°K)	$-dH_{c2}/dT$ (kG/°K)	l_{eff} (Å)	$(\xi_0 l_{\text{eff}})^{1/2}$ (Å)	κ
2.13	60	2	1	27	490	7.8
2.18	160	6	3	10	290	23
2.31	520	8	8	3.1	160	33
2.18	1000	17	15	1.6	120	73

The integral equation for G_n as a function of frequency $\omega = iE_j = i\pi(2j+1)k_BT$, $j = 0, \pm1, \pm2\cdots$, and momenta $\vec{p}$ and $\vec{p}'$ is[7]

$$G_n(\vec{p},\vec{p}';iE_j) = G_0(p;iE_j)\delta(\vec{p}-\vec{p}') + (2\pi)^{-3}G_0(p;iE_j)\int d^3p''\, V(\vec{p}-\vec{p}'')G_n(\vec{p}'',\vec{p}';iE_j), \quad (1)$$

where $G_0(p;iE_j) = (iE_j - \epsilon_p)^{-1}$ is the Green's function for a noninteracting Fermi gas. Here $\epsilon_p = (\hbar^2p^2/2m - E_F)$ is the single-particle energy[8] relative to the Fermi energy E_F, and $V(\vec{q})$ is the Fourier transform of the tunneling potential $V(\vec{r})$. For simplicity we choose to represent the tunneling barriers by an array of two-dimensional delta-function potentials of equal strength, $V(\vec{r}) = V\sum_n \delta(z-z_n)$. The quantity z_n represents the positions of the barriers, which are oriented perpendicular to the z axis. We shall assume that the barriers are spaced an average distance d apart, but with sufficient randomness so that the mean uncertainty in the distance between any two barriers is large compared to the Fermi wavelength. This assumption is analogous to that of a completely random distribution of impurities in the ordinary dirty metal case[9] and is necessary to avoid resonance effects that can occur in a perfectly periodic array. As a result of this simplification, only double interactions with the same tunneling barrier are important since all others vanish upon averaging over the spacing between barriers. It can then be readily shown that the Green's function is given by

$$G_n(\vec{p},\vec{p}';iE_j) = \delta(\vec{p}-\vec{p}')[iE_j - \epsilon_p - \Sigma(p_\parallel;iE_j)]^{-1}, \quad (2)$$

where

$$\Sigma(p_\parallel;iE_j) = (V^2/d)g_n(p_\parallel|0;iE_j) \quad (3)$$

is the electron self-energy. In Eqs. (2) and (3), $p_\parallel$ is the component of momentum parallel to the barriers and $g_n(p_\parallel|z;iE_j)$ is the one-dimensional Fourier transform of $G_n(\vec{p};iE_j)$.

For particles at the Fermi surface Eqs. (2) and (3) yield the result

$$\text{Im}\Sigma(0;iE_j) = -E_F\,\text{sgn}E_j/p_F l_{\text{eff}},$$
$$\text{Re}\Sigma(0;iE_j) = 0, \quad (4)$$

where

$$l_{\text{eff}} = dt/(1-t) \quad (5)$$

is an effective mean free path, p_F is the Fermi wave number, and we have expressed the strength V in terms of the transmissivity $t = [1 + (V/\hbar v_F)^2]^{-1}$ for a plane wave normally incident on a single delta-function barrier. In Eq. (4) we have assumed that $p_F l_{\text{eff}} \gg 1$ and have therefore kept only terms of order[10] $E_F(p_F l_{\text{eff}})^{-1}$. Furthermore, we have considered only those quasiparticles whose momentum $\vec{p}$ is essentially perpendicular to the barriers ($p_\parallel \approx 0$). Because of their small probabilities for transmission, the remaining quasiparticles contribute little to the transport process.

The above calculation shows that the normal-metal Green's function is characterized by an effective mean free path l_{eff}, and thus, the construction of the Gor'kov kernel proceeds exactly as in the case of randomly distributed impurity atoms.[11] The result is a Ginzburg-Landau equation with an effective coherence length $\xi(T)$. In the "dirty" limit $l_{\text{eff}} \ll \xi_0$ (the Pippard coherence length), the coherence distance $\xi(T)$ near T_c is given by[11]

$$\xi(T) = 0.85[\xi_0 l_{\text{eff}} T_c/(T_c - T)]^{1/2}, \quad (6)$$

and the critical field H_{c2} is given by

$$H_{c2}(T) = \Phi_0/2\pi\xi^2(T), \quad (7)$$

where Φ_0 is the flux quantum. Since we are concerned with critical fields near T_c where $H_\perp$ is small, we are justified in ignoring the effect of paramagnetic quenching.[12] At $T=0$, Eq. (6) for $\xi(T)$ is, apart from a factor of order unity, in agreement with the result of Parmenter.[5]

In order to calculate H_{c2}, we must first determine the quantities l_{eff} and ξ_0 for the four measured samples. Since the granular metal is characterized by an effective mean free path, the normal resistivity is given by the usual relation: $(\rho_n l_{\text{eff}})^{-1} = \frac{2}{3}N(0)v_F e^2$, where $N(0)$ is the density of electronic states at the Fermi surface. Using the value[13] $\frac{2}{3}N(0)v_F e^2 = 6.3\times10^{10}$ Ω^{-1} cm^{-2}, determined from skin-effect measurements on pure Al, and the measured values of ρ_n, we obtain the values of l_{eff} given in Table I. Also listed are the values of the quantity $(\xi_0 l_{\text{eff}})^{1/2}$. The Pippard coherence length $\xi_0 = \hbar v_F/\pi\Delta$ used was obtained by multiplying the values[14] $\xi_0 = 16\,000$ Å for pure Al by the ratio of the energy gap Δ of pure Al to the energy gap of the granular film. The energy gaps were determined from tunneling measurements. Using these values of $(\xi_0 l_{\text{eff}})^{1/2}$ in Eqs. (6) and (7) results in the slopes dH_{c2}/dT given in the table. The agreement between the theoretical and measured values of the slopes is good. The agreement is good even for the film with $l_{\text{eff}} = 1.6$ Å, for which $p_F l_{\text{eff}} \sim 1$. In the last column of Table I we have listed the values of the Ginzburg-Landau parameter $\kappa = H_\perp(T)/\sqrt{2}H_c(T)$ near T_c. The thermodynamic critical field $H_c(T)$ was assumed to follow the law $H_c(T) = H_c(0)[1-(T/T_c)^2]$. The quantities $H_c(0)$ were obtained by multiplying $H_c(0)$ for pure aluminum by the ratio of the energy gaps of the granular film to that of pure aluminum. Large critical fields, attributed to small grain size, have also been reported for tungsten[15] and niobium and tantalum.[16] These results can be interpreted in terms of the present theory.

It should be remarked that the result Eq. (6) relies on coherence between quasiparticles extending over many grains [$\xi(T) \gg d$]. This condition will be satisfied if the transmissivity of the barriers is sufficiently large. As can be seen from the values of $(\xi_0 l_{\text{eff}})^{1/2}$ given in Table I, the condition $\xi(T) \gg d$ was well satisfied for our films. For the values of l_{eff} in the table, the range of t computed from Eq. (5) is $0.04 < t < 0.4$, indicating that the coupling between grains is indeed very strong. In the limit of very weak coupling between grains ($t \to 0$), one would expect the critical field to approach that of an isolated grain.[17]

The results of the present work enable us to make the following statements regarding some of the mechanisms that have been proposed to explain the enhancement of T_c. The finding that the grains are strongly coupled to each other appears to rule out enhancement due to quantization of electronic motion expected in small isolated systems.[18] If the enhancement of T_c were due to Jospehson tunneling between grains,[6] one would expect T_c to vary rapidly with transmissivity t. This is not observed experimentally. As can be seen from Table I, T_c is virtually independent of t. However, this result does not allow us to rule out Parmenter's mechanism, because another effect may be present which tends to reduce T_c. Other possible mechanisms for the rise in T_c include surface enhancement of the effective electron-phonon interaction[1,3] and an increase in the electronic density of states due to atomic disorder. More experimental and theoretical work is required to determine unambiguously the predominant mechanism of the enhancement of T_c.

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[5]R. H. Parmenter (private communication) has shown that, at $T=0$, the effective coherence length of Ref. 4 is proportional to the geometric mean of the conductivity mean free path and the Pippard coherence length. The proportionality constant is $(\pi/4)(\lambda/3)^{1/2}$, where λ is the dimensionless BCS coupling constant. Parmen-

ter's analysis can be extended to finite temperatures.

[6]Ref. 4, footnote 14a.

[7]See, for example, A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, Quantum Field Theory in Statistical Physics (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), p. 328.

[8]It is assumed that there is no scattering within a given grain, and the electronic energy spectrum of pure Al can be represented by that of free electrons with an effective mass m.

[9]See Ref. 7, pp. 329-341.

[10]It can be shown that terms of order $E_F(p_F l_{eff})^{-2}$ give rise to an increased density of electronic states $N(0)$. Such an effect could result in an enhanced T_c.

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STUDY IN AMMONIUM DIHYDROGEN PHOSPHATE OF SPONTANEOUS PARAMETRIC INTERACTION TUNABLE FROM 4400 TO 16 000 Å

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This Letter reports the quantitative experimental study of tunable parametric amplification of quantum noise in ammonium dihydrogen phosphate (ADP). Because of phase-matching conditions the parametric noise output is limited to narrow spectral regions which could be tuned from 4400 to 16 000 Å by simply rotating the ADP crystal around the pump-beam direction. A complete study of the physical parameters which determine this spontaneous parametric interaction was made and the results compared with theory. The results are also of practical interest (a) because the observed small levels of output represent the noise level of parametric light amplifiers and (b) because the measured gain allows predictions about the construction of tunable coherent light oscillators in the visible.

The extension of tunable parametric output through the visible and the direct measurement of various physical parameters of single-passage amplification without the use of external mirrors differentiates the reported measurements from previous observations of tunable parametric oscillators. Powerful coherent output in the infrared and far red using an optical cavity and a pump at 5300 Å has been observed by Giordmaine and Miller[1] and Miller and Nordland[2] in $LiNbO_3$ and by Akhmanov et al.[3] in potassium dihydrogen phosphate.

In the present arrangement the pump beam at 3472 Å, consisting of 1-MW pulses of 20-nsec duration, traversed the ADP crystal at near-normal incidence. After attenuation of the pump light by appropriate filters, parametric signal and idler radiation was detected at a distance of about 2 m by a monochromator-photomultiplier system. The presence of signal or idler output was established by an increase of signal over background radiation (mainly due to luminescence from the cutoff filters) as the crystal was rotated through the phase-matching orientation for a preselected wavelength. From the position of these peaks the tuning curve of Fig. 1 was obtained. The tuning range of 4400-16 000 Å is limited by the onset of optical absorption by ADP in the infrared. The spectral sensitivity of the photomultiplier confined the observable part of the tuning range to 4400-10 000 Å. The dashed curve of Fig. 1 shows a quadratic dependence of the change in crystal orientation $\Delta\theta$ on the