Ordinarily the largest effect produced by doping a pure material would be to drastically reduce a. (Such is the case for Guénault's purer samples.) This reduction is not important when a is already much less than one.

We wish to call attention to the fact that we have ignored anisotropy in the normal density of states. This quantity enters both in the gap equation and in the equation for thermal conductivity, where it really enters twice: in the number of carriers and in their mobility. A more complete theory will have to take account of this.

ACKNOWLEDGMENTS

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APPENDIX

Equation (V.3) expresses the dependence on τ of the anisotropic part of the gap, Δ_1. We here outline a derivation of (V.3). To understand the derivation the reader should already be familiar with the article by Hohenberg.[6]

Hohenberg's Eq. (31) says, in our notation,

$$\Delta_{\min}(l)\approx\Delta_{\min}(\infty)\{1+\langle a^2\rangle^{1/4}/(2\tau\Delta_0)\}\,. \qquad \text{(A1)}$$

But $\Delta_{\min}(\infty)=\Delta_0[1+a_{\min}]$. This is a definition of $a_{\min}$, the value of $a(\Omega)$ for the direction (Ω) in which the gap has its minimum value. We are interested in a linear approximation for the decrease in Δ_1 between $\tau=\infty$ and $\tau=$ the value at which $\Delta_1\rightarrow 0$ in this approximation. We therefore find the value of τ for which $\Delta_{\min}(l)\approx\Delta_0$ and Eq. (V.3) immediately follows. Hohenberg's Fig. 2 shows that this result is fairly good for all directions Ω. Equation (V.3) results from an approximation which coalesces the effects of doping on a complex gap into the real part alone.

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Mixed State of Type-I Superconducting Films in a Perpendicular Magnetic Field

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Thin films of type-I superconductors are shown to exist in a variety of quite distinct mixed states, depending on their thicknesses. The most interesting of these states consist of hexagonal arrays of vortices of larger than unit quantum number. Their general character falls between that of the ordinary mixed state, a triangular array of unit vortices which occurs for sufficiently thin films, and the intermediate states consisting of islands of superconducting phase in a matrix of normal phase which occurs for sufficiently thick films. The theory is developed in Abrikosov's high-field approximation, which gives solutions of the Ginzburg-Landau equations that are exact in the limit as the applied field approaches the second critical field H_{c2}. Two critical thicknesses are found and determined as functions of the Ginzburg-Landau parameter κ. The first and smaller critical thickness is the maximum film thickness for which the ordinary mixed state will exist near H_{c2}. The second critical thickness is the maximum for which a second-order field transition occurs at H_{c2}. The new types of mixed state are stable for values of film thickness intermediate between these two.

INTRODUCTION

A THEORETICAL model given by Tinkham[1] has indicated that sufficiently thin type-I films assume the mixed state when placed in a magnetic field normal to their surface. Maki[2] has recently shown that the Ginzburg-Landau (GL) equations predict this. He derived an approximate value for the maximum thickness a film may have in order that it should have a second-order transition to the mixed state at the upper critical field H_{c2}. We have looked in greater detail at the solutions of the GL equations in the neighborhood of the upper critical field using Abrikosov's high-field approximation[3] properly modified as in Maki's paper to take into account the field energy. In brief, our results, which apply near H_{c2}, are that very thin films exist in the state consisting of a triangular array of vortices which was first determined by Kleiner, Roth, and Autler (KRA).[4] Films of intermediate thickness, however, make a second-order transition as the field is decreased

[1] M. Tinkham, Phys. Rev. **129**, 2413 (1963); Rev. Mod. Phys. **36**, 268 (1964). Experiments on narrow strips of Sn by R. D. Parks and J. M. Mockel, Phys. Rev. Letters **11**, 354 (1963), show structure in resistance versus perpendicular magnetic field due to the presence of vortex structure. J. Pearl, Appl. Phys. Letters **5**, 65 (1964), discusses a model for such vortices and the forces between them.

[2] Kazumi Maki, Ann. Phys. (N. Y.) **34**, 363 (1965).

[3] A. A. Abrikosov, Zh. Eksperim. i. Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet. Phys.—JETP **5**, 1174 (1957)].

[4] W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. **133**, A1236 (1964).

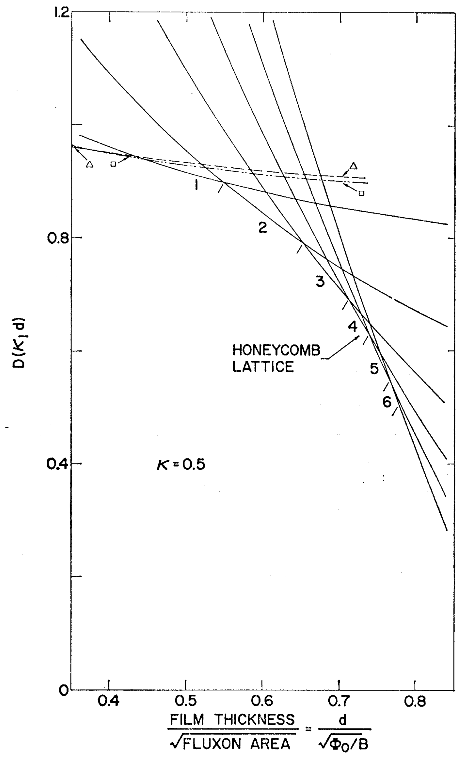

FIG. 1. The function $D(\kappa,d)$ where $\kappa=0.5$, defined by (6) and giving the free energy (7) corresponding to various solutions of the linearized GL equation (1).

through H_{c2} onto one of a variety of states depending on their value of GL parameter κ and thickness. Still thicker films will make a transition into an intermediate state at field magnitudes greater than H_{c2} but less than the bulk critical field H_c.

DERIVATION OF HIGH-FIELD APPROXIMATION

Consider the two-dimensional periodic solutions of the linearized GL equation.[3]

$$[(i/\kappa)\boldsymbol{\nabla}+\mathbf{A}_0]^2\psi(x,y)=\psi\,,\quad \mathrm{curl}\mathbf{A}_0=B\hat{z}\,,\qquad (1)$$

where B is the average flux density and equals the applied field for a thin film in a perpendicular magnetic field. The z dependence of ψ for $B\approx H_{c2}$ may be neglected because the solutions of Eq. (1) depending on z have eigenvalues corresponding to much smaller values of B. They therefore give corrections to ψ which vanish as B approaches H_{c2}.[5]

We will use solutions of the linearized GL equation and determine their magnitude by minimizing the GL free-energy functional including the inhomogeneous fields generated by the supercurrents of those solutions. This procedure is equivalent to Abrikosov's approximation for the bulk type-II mixed state in the neighborhood of H_{c2}, provided we replace the right-hand side of Eq. (1) by $(B/\kappa)\psi$ which gives ψ the unit-cell area appropriate to the average flux density B, and provided we include the remaining term $[1-(B/\kappa)]\psi$ in the free energy.

We have found it convenient to work in terms of the Fourier components $g_{\mathbf{k}}$ of the absolute square of the order parameter satisfying (1),

$$|\psi(x,y)|^2=N\omega(x,y)=N\sum_{\mathbf{k}} g_{\mathbf{k}}e^{i\mathbf{k}\cdot\rho}\,,\qquad (2)$$

where ω is normalized to have a two-dimensional space average of unity, $g_0=1$, ρ is the two-vector (x,y), and the magnitude N of ω is to be determined. The field which is produced by the supercurrents implied by the order parameter (2) and the vector potential $\mathbf{A}_0$ can be written exactly in terms of these coefficients,[6]

$$\begin{aligned}H(r)-B\hat{z}=(N/2\kappa)\{-\theta(z)[\omega(x,y)-1]\hat{z}\\+\sum_{\mathbf{k}}{}'(g_{\mathbf{k}}/2k)\boldsymbol{\nabla}[\exp(i\mathbf{k}\cdot\boldsymbol{\rho}-k|z-\tfrac{1}{2}d|)\\-\exp(i\mathbf{k}\cdot\boldsymbol{\rho}-k|z+\tfrac{1}{2}d|)]\}\,,\qquad (3)\end{aligned}$$

where the primed summation excludes the term with $\mathbf{k}=0$, and $\theta(z)=1$ for $d/2>z>-d/2$ and zero otherwise, and k is the magnitude of the vector $\mathbf{k}$.

By substituting these expressions for the order parameter and magnetic field into that for the GL free energy[3] and integrating over all values of z and a unit area in the x,y plane, we obtain the density of free energy in the x,y plane,

$$\begin{aligned}\langle\Delta F-B^2\rangle=-Nd[(\kappa-B)/\kappa]+\tfrac{1}{2}N^2d[\beta-(\tfrac{1}{2}\kappa^2)\textstyle\sum'|g_{\mathbf{k}}|^2\\\times(e^{-kd}-1+kd)/kd]+d\langle\mathbf{A}_p{}^2|\psi|^2\rangle\,,\qquad (4)\end{aligned}$$

where β is the average of ω^2, $\beta=\sum|g_{\mathbf{k}}|^2$, and $\mathbf{A}_p=\mathbf{A}-\mathbf{A}_0$ is the periodic part of the vector potential with $\mathrm{div}\mathbf{A}_p=0$ and $\langle\mathbf{A}_p\rangle=0$. The final term of the above expression has the integration only symbolically indicated by the angular brackets. When this term is neglected, the free energy (4) has its minimum for

$$N=(\kappa-B)/\kappa D(\kappa,d)\,,\qquad (5)$$

where

$$D(\kappa,d)=\beta-(1/2\kappa^2)\textstyle\sum'|g_{\mathbf{k}}|^2(e^{-kd}-1+kd)/kd\,,\qquad (6)$$

with the result

$$\langle\Delta F-B^2\rangle=-d(\kappa-B)^2/2\kappa^2D(\kappa,d)\,.\qquad (7)$$

[5] G. Eilenberger, Z. Physik **180**, 32 (1964) and subsequently G. Lasher [Phys. Rev. **140**, A523 (1965)] have shown that Abrikosov's approximation for the mixed state in bulk type-II specimens near H_{c2} is the lowest order term in an expansion of the exact solution in powers of $(H_{c2}-B)/B$. (The author regrets not being aware of Dr. Eilenberger's work at the time of publication of his paper.) F. M. Odeh (to be published) has proved that such expansions converge and indeed represent the exact solutions of the full nonlinear GL equations. The same type of series solutions could be found for our case of type-I thin films. The terms arising from the z dependence of the order parameter would give corrections to the absolute square of the order parameter and to the free energy of order $[(H_{c2}-B)/B]^3$.

[6] The first term gives curl $H=j$ inside the film according to Eq. (7) of Ref. 8 (but note the difference in units), and the second term makes div$H=0$ at the surfaces of the film.

DISCUSSION OF RESULTS

The last equation tells us that a film will make a transition to that solution of the linearized equation which has the smallest value of the function $D(\kappa,d)$. In Fig. 1 we plot $D(\kappa,d)$ for $\kappa=0.5$ versus $d/(\Phi_0/B)^{1/2}$ as computed from the g_k for several states. The line indicated by a triangle represents the KRA triangular lattice function, and it lies lowest for $d(\Phi_0/B)^{1/2}$ less than 0.37. At that point it is intersected by the line representing Abrikosov's original square lattice of vortices marked with a square. This value of d is then a critical value in the sense that only films with a smaller thickness have the usual KRA mixed state. This critical film thickness is given for all values of κ in the upper curve of Fig. 2.

In order to determine the equilibrium state for thicker films we have evaluated $D(\kappa,d)$ for states consisting of vortices arranged on all of the primitive lattices as well as the hexagonal lattice[7] which has two vortices per unit cell. The same lattices of vortices with higher than unit quantum number were also considered. We have previously given the transformation which gives the order parameter of a state consisting of vortices of quantum number ν in terms of that of the state of unit quantum-number vortices on the same lattice[8]:

$$\Psi^{(\nu)}(\rho)=[\Psi^{(1)}(\rho/\sqrt{\nu})]^{\nu}. \quad (8)$$

As the film thickness is increased, past this first critical value a complicated sequence of these states becomes the preferred state. The free-energy differences between the various states in this range are so small and the identity of the preferred state persists for such small ranges of film thickness that they would be very difficult to observe in real films. This region appears shaded in Fig. 2.

For still greater thicknesses the preferred state consists of vortices of increasing quantum number on the hexagonal lattice as shown in Fig. 1, and the absolute square of the $\nu=2$ state is shown in Fig. 3. Only the first six of this sequence of states are shown in the figure, but we can argue that the complete sequence has an envelope which intersects the $D=0$ axis at a value of $d/(\Phi_0/B)^{1/2}$ of 0.83. The other lattices give similar sequences of curves with the same intersection for the envelope, but lying above the curves of the hexagonal lattice.

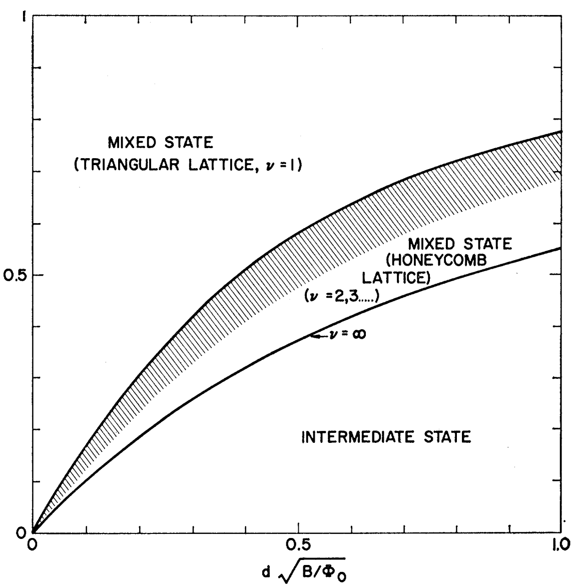

FIG. 2. Critical values of $2\kappa^2$ versus film thickness d. The upper curve traces those values of d and κ which give equal values of the free energy for the triangular and square lattice solutions. In the shaded area a large number of solutions, not indicated in Fig. 1, have the lowest free energy for small ranges of the parameters. In the next region below that the equilibrium states are the sequence of states of vortices on a hexagonal or honeycomb lattice with the vortex quantum number going to infinity as one approaches the lower curve.

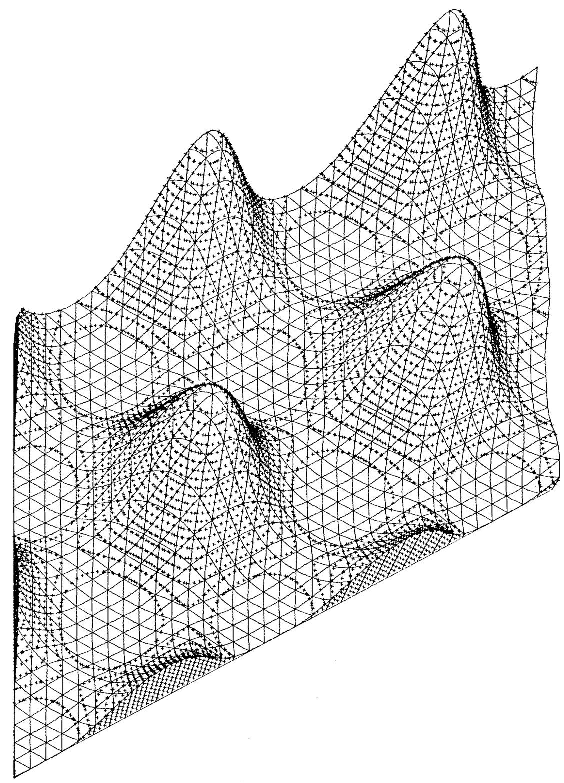

FIG. 3. A perspective drawing of the absolute square of the order parameter $\omega(x,y)$ versus x and y for a hexagonal lattice of $\nu=2$ vortices. The contour interval is 0.2 in units such that ω average is unity.

[7] Taking $B=\kappa$ in Eq. (1) we may write the solution consisting of unit fluxoids on a hexagonal lattice as $\sum \exp\frac{1}{2}\pi\kappa^2[iR\times\rho-\frac{1}{2}(R-\rho)^2]$ where the sum is over the primitive lattice vectors R of the *triangular* lattice having twice the area corresponding to a quantum of flux. After some manipulation the Fourier coefficients g_k of the absolute square of this solution may be shown to be proportional to $\exp(-k^2/8\pi\kappa^2)\sum \exp[-i(q\times k)/2\pi\kappa^2]\exp[(q-\frac{1}{2}k)^2/2\pi\kappa^2]$, where k and q are reciprocal lattice vectors and the sum is over all q.

[8] G. Lasher, Ref. 5.

This second critical thickness where $D(\kappa,d)$ vanishes as the fluxoid quantum number approaches infinity can be found from the following argument. The transformation of Eq. (8) accentuates the absolute value of the order parameter at its maximum compared to its value at other positions in the unit cell. In the limit of large ν the absolute square of the order parameter approaches an array of two-dimensional Gaussians of the form $\exp(-\frac{1}{2}\kappa B\rho^2)$ whose centers fall on the lattice dual to the lattice of vortices and with a unit-cell area proportional to ν. For large values of ν one may neglect the overlap of these Gaussians as is already apparent from Fig. 3 for $\nu=2$. The second critical thickness can, therefore, be found by evaluating $D(\kappa,d)$ for the above Gaussian form[9] and setting the resulting expression equal to zero. The result is indeed independent of the area of the unit cell as this area approaches infinity and gives the condition

$$2\kappa^2-1=(\sqrt{\pi}/2\delta)[1-\exp(\delta^2)\operatorname{erfc}(\delta)],$$

where

$$\delta=(\tfrac{1}{2}\pi)^{1/2}d/(\Phi_0/H_{c2})^{1/2}. \tag{9}$$

This second critical thickness is plotted as the lower curve of Fig. 3, and we will argue that this is the dividing line between films which have the mixed state near H_{c2} and those which have the intermediate state.

There is one respect in which the behavior of the high-quantum-number mixed states will differ from the $\nu=1$ states. They have a much larger maximum value of $|\psi|^2$ for a given average value and, therefore, will be distorted by the effect of the nonlinear terms in the GL equations at much smaller values of $(\kappa-B)/\kappa$ than is the case for the $\nu=1$ solution. That is, the simple B dependence of Eqs. (5) and (7) will hold for smaller ranges of B.

We will briefly consider the nature of the normal-superconducting transition with decreasing field for film whose thickness is slightly greater than the second critical thickness, i.e., slightly into the intermediate-state range where $D(\kappa,d)$ has negative values for large ν. For values of the field not too different from $H_{c2}=\kappa$ in these units, we can use the free-energy expression (4) including the third term which is proportional to N^3 and predict that there would occur a first-order transition to this state at a field between H_{c2} and the bulk critical field. One must, however, consider not a single given state but rather must find which one of all the states will give the largest value for the transition field. We believe that the transition will occur into a state similar to our high-quantum-number states and thus resemble the intermediate state discussed by Davies[10] consisting of islands of superconductivity surrounded by the normal phase. This discussion also predicts that critical field versus thickness will begin increasing as the film thickness increases past our second critical thickness.

To our knowledge, there exists no experimental data to compare quantitatively with these predictions. Cody and Miller[11] have recently obtained a curve of critical field versus film thickness for Pb at 4.2°K. The value of film thickness indicated by the cusp in this curve is, we believe, of the same nature as the critical thickness of Eq. (9), but the GL theory does not apply at such low temperatures nor has any theory of the correction of GL theory to the required order in Ψ and for a relatively clean material been given. The critical thickness observed by Cody and Miller was 9000 Å, whereas Eq. (9) with $\kappa=0.5$ and $H_{c2}=400$ G gives 1900 Å.

Results on Sn films by tunneling have been given by Collier and Kamper,[12] but most of their film thicknesses fall below our critical value and thus their observation of a second-order transition at H_{c2} is merely consistent with our predictions. Their thickest film has parameters which fall in the region of our high-fluxoid-number solutions. Whether this accounts for the different results for this film can only be convincingly demonstrated by a considerable extension of our work to apply it to values of the field much less than the critical field. The slope of their measured tunneling resistance versus field does appear to be somewhat greater at H_{c2} for this film, and this is consistent with out smaller value of $D(\kappa,d)$ for the higher quantum number solutions.

ACKNOWLEDGMENTS

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[9] If Maki had used this expression in his "local kernel" [his Eq. (15)] instead of $\exp(-\kappa Bx^2)$ his result would, we believe agree exactly with Eq. (9).

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