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A POSSIBLE HYPO-CRITICAL POINT IN THE PHASE DIAGRAM OF A MODERATELY SMALL SUPERCONDUCTOR IN A MAGNETIC FIELD

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CONTENTS

An expression for the difference in Gibbs free energy between the superconducting and normal states of a moderately small superconductor, in terms of ψ, the wave function of the superconducting electrons, has been applied to experimental observations on the transitions of tin whiskers (Bibby, Nabarro, McLachlan & Stephen, 1974, preceding paper) and fails if the coefficient of the term in ψ^6 is negative at the Landau critical point. It is suggested that a term of order ψ^8 be incorporated, with a positive coefficient. It is shown that this gives rise to a transition from the normal state to a superconducting state with a finite value of ψ at a point (H'', T''), denoted the hypo-critical point since it occurs at a lower field than does the Landau critical point. The phase boundary describing this transition branches at a finite angle from that describing the second order transition at lower fields, the ratio of these slopes, for a cylinder in parallel field, being less than or equal to 1.32.

1. Introduction

The transition from the superconducting to the normal state of a moderately small specimen in a longitudinal magnetic field H may be thermodynamically of second order if it occurs sufficiently close to the critical temperature T_c (Silin 1951; Ginzburg 1958). Bibby *et al.* (1974) (hereafter B.N.M.S.) examined the change from a second order to a first order transition both theoretically and experimentally. They predicted that the change should occur at a critical point of the type discussed by Landau (1935). The supercooling curve in the (H, T) plane for the first order region should be the prolongation of the equilibrium transition curve for the second order region, while the thermodynamic equilibrium transition curve for the first order region should branch tangentially from this curve. The first prediction was verified experimentally. The second was not; the two transition curves meet at a finite angle.

B.N.M.S. assumed that their samples were small enough for the Ginzburg–Landau superconducting wave function ψ to be uniform throughout the sample, and took ψ to be real. They expressed the excess G of the free energy per unit volume over that of the normal state by

$$G = -A\psi^2 + \tfrac{1}{2}B\psi^4 + \tfrac{1}{3}C\psi^6, \tag{1.1}$$

where $A = a_1 - a_2H^2, \quad B = b_1 - b_2H^2$

and

$$C = c_1 + c_2H^2. \tag{1.2}$$

Here a_1 and b_1 are the usual Ginzburg–Landau parameters, a_1 being assumed to be of the form $a(T_c - T)/T_c$, b_1 and c_1 being assumed independent of temperature. The quantities a_2, b_2 and c_2 are purely geometrical, and for a circular cylinder of radius r are proportional to r^2, r^4 and r^6 respectively. The coefficient c_1 was introduced in an attempt to produce a theory which was self-consistent to order ψ^6. With the exception of the new material constant c_1, all the coefficients $a_1, \ldots, c_2$ are known to be positive. B.N.M.S. give experimental and theoretical evidence that c_1 is negative, and we write

$$\gamma = -c_1 > 0. \tag{1.3}$$

B.N.M.S. show that, if $c_1 < 0$, C will necessarily be negative at the Landau critical point for rather large samples. We now suggest that in this case the Landau critical point will be masked by a branch point in the phase diagram which we call a hypo-critical point, because it occurs at a magnetic field H'' below that, H', of the Landau critical point.

2. Theory of the hypo-critical point

We use the notation of B.N.M.S. When $C < 0$ at the Landau critical point, the Gibbs free energy G given by (1.1) becomes, at this point, $G = -\frac{1}{3}|C|\psi^6$, and no stable equilibrium is possible. Solutions are possible only if we add to the expression (1.1) a term $\frac{1}{4}D\psi^8$, with $D > 0$. We note that the formulae of Brandt (1973) do indeed give $D > 0$ for $H = 0$ and $T < T_c$, and we assume that $D > 0$ in the whole range $T' \leqslant T < T_c$, while $C < 0$ in the same range. In the spirit of a Landau approximation, we shall neglect the variation of D with H and T in this range. Since we may be concerned with the case in which the condition $C > 0$ only just fails to be fulfilled, we shall continue to take account of the variation of C with H. Then, in the normalization of B.N.M.S., we have

$$g/8\pi = a_2(h^2 - \delta t)\,\psi^2 + \tfrac{1}{2}b_2(1-h^2)\,\psi^4 + \frac{1}{3b_1}(-b_2\gamma + b_1c_2h^2)\,\psi^6 + \frac{b_2D}{4b_1}\psi^8. \tag{2.1}$$

All the coefficients in this expression are positive. At the Landau critical point (which is no longer a point of physical interest) there is a 'strongly superconducting' state with a minimum of energy determined by the conditions $\partial g/\partial\psi^2 = 0$ and $h^2 = \delta t = 1$, lying at

$$\psi^2 = (b_2\gamma - b_1c_2)/b_2D > 0, \tag{2.2}$$

with

$$g/8\pi = -(b_2\gamma - b_1c_2)^4/12b_1b_2^3D^3 < 0. \tag{2.3}$$

We abbreviate (2.1) into the same form as (2.10) of B.N.M.S., namely

$$g/8\pi = -\boldsymbol{A}\psi^2 + \tfrac{1}{2}\boldsymbol{B}\psi^4 + \tfrac{1}{3}\boldsymbol{C}\psi^6 + \tfrac{1}{4}\boldsymbol{D}\psi^8. \tag{2.4}$$

For suitable values of h and δt the strongly superconducting state will be in thermodynamic equilibrium with the normal state. The conditions for this are

$$g = 0, \tag{2.5}$$

$$\partial g/\partial\psi = 0 \tag{2.6}$$

and

$$\psi^2 > 0. \tag{2.7}$$

We write these in the form

$$-A+\tfrac{1}{2}B\psi^2+\tfrac{1}{3}C\psi^4+\tfrac{1}{4}D\psi^6 = 0 \tag{2.8}$$

and

$$-A+B\psi^2+C\psi^4+D\psi^6 = 0, \tag{2.9}$$

and solve (2.8) and (2.9) simultaneously to obtain

$$\psi^2 = (6BC+81AD)/(27BD-8C^2). \tag{2.10}$$

Substituting this value of ψ^2 in (2.8) or (2.9), we obtain the equation of the curve of equilibrium between the normal state and the strongly superconducting state in the form:

$$324ABCD-64AC^3+729A^2D^2-12B^2C^2+54B^3D = 0. \tag{2.11}$$

There exists a field H'' below H' at which the normal state, the usual weakly superconducting state and the strongly superconducting state are all in thermodynamic equilibrium. We call this point (H'', T'') the hypo-critical point. Since equilibrium between the normal and the weakly superconducting states below the Landau critical point requires that $A = 0$ and $B > 0$, while we have assumed that $C < 0$ in this region, (2.11) reduces at this point to

$$2C^2 = 9BD, \tag{2.12}$$

or

$$2(b_2\gamma-b_1c_2h''^2)^2 = 9b_1b_2{}^2D(1-h''^2). \tag{2.13}$$

If we eliminate D between (2.10) and (2.12) and remember that $A = 0$ at the hypo-critical point, we obtain at this point

$$\psi^2 = -3B/2C > 0. \tag{2.14}$$

We discuss the solutions of (2.13) by means of figure 1, in which the parabola represents the term on the left of the equation, independent of D, while the straight lines through the point $h''^2 = 1$ have slopes proportional to $-D$.

We first notice that there is a restriction on the coefficients in (2.1). The point $h = 0$, $\delta t = 0$ must be the observed transition temperature in the absence of an applied field, so that the value of g at this point must be positive for any value of $\psi^2 > 0$. The condition for this is that

$$D > 2\gamma^2/9b_1. \tag{2.15}$$

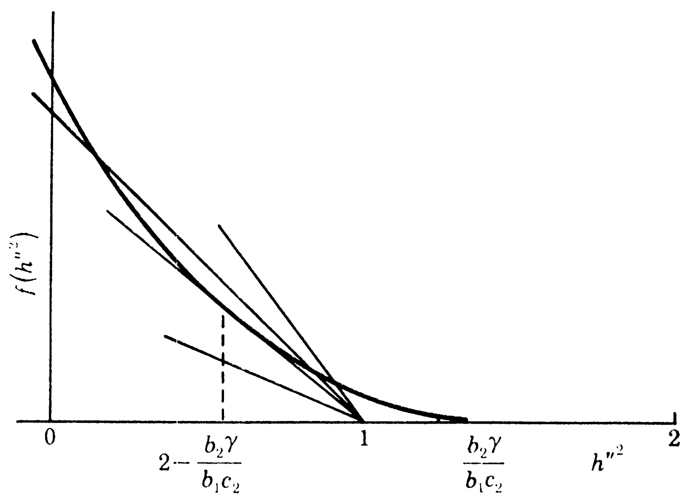

FIGURE 1. Graphical solution of equation (2.13). The parabola is independent of the coefficient D, while the straight line passes through the fixed point (1, 0) with a negative slope proportional to D.

But the condition that (2.13) should have a zero root in h''^2 is

$$D = 2\gamma^2/9b_1, \tag{2.16}$$

the other root being

$$h''^2 = (2b_1c_2 - b_2\gamma)\, b_2\gamma/b_1^2c_2^2. \tag{2.17}$$

Provided that h''^2 given by (2.17) is positive, i.e. provided that $b_2\gamma < 2b_1c_2$, this is the larger root of (2.13), and increases with D. We note also that for very fine samples, where c_2 is very small, the value of h''^2 given by (2.13) tends to the finite limit $1 - 2\gamma^2/9b_1D$.

By sketching (2.4) with $A = 0$, $B > 0$, $C < 0$ and $D > 0$ we readily see that any root of (2.12) or (2.13) corresponds to a *minimum* of $g(\psi^2)$, so that any positive root in h''^2 represents a stable physical state, since the positive sign of ψ^2 is assured by (2.14).

The necessary and sufficient conditions for the existence of a hypo-critical point are thus

$$2b_1c_2 > b_2\gamma > b_1c_2 \tag{2.18}$$

and (2.15), and the field h'' at the hypo-critical point lies in the range given by

$$1 \geqslant h''^2 \geqslant (2b_1c_2 - b_2\gamma)\, b_2\gamma/b_1^2c_2^2. \tag{2.19}$$

We now look for possible intersections between the curve (2.11) and the thermodynamic equilibrium curve in the first order region, (4.6) of B.N.M.S., which in our present notation becomes

$$3\boldsymbol{B}^2 = 16\boldsymbol{AC}. \tag{2.20}$$

Eliminating $\boldsymbol{A}$, we find that (2.11) and (2.17) intersect where

$$64\boldsymbol{C}^2 = 243\,\boldsymbol{BD}. \tag{2.21}$$

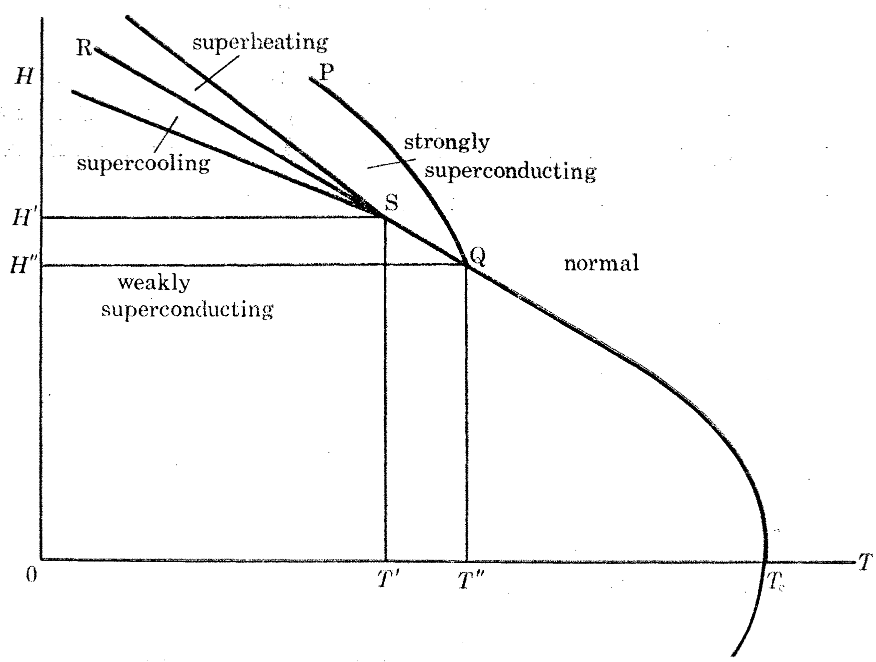

FIGURE 2. The predicted phase diagram in the (H, T) plane, showing the second order transition branching into supercooling, thermodynamic equilibrium and superheating curves at the Landau critical point $S(T', H')$. These boundaries are masked by the strongly superconducting state, which begins at $Q(T'', H'')$. The phase boundary PQ between the normal and the strongly superconducting states branches from the second order boundary T_cQ at a slope which is θ times the slope of the latter at the point Q.

This is of the same form as (2.12) or (2.13), and can have no roots in the region of the ordinary first order transition, where $h^2 > 1$.

The phase diagram therefore takes the form of figure 2, the curve PQ of (2.11) replacing the curve RS of (4.6) of B.N.M.S.

We determine the slope of the curve of (2.11) at the hypo-critical point by setting, in analogy with (4.10) of B.N.M.S.,

$$h^2 = h''^2 + \epsilon\theta \quad \text{and} \quad \delta t = h''^2 + \epsilon \tag{2.22}$$

and inserting these values into (2.11), expressing $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$ and $\boldsymbol{D}$ in terms of h^2 and δt by comparison of (2.1) and (2.4). The terms independent of ϵ vanish because h''^2 is a root of (2.13). Using (2.13) again to eliminate D, we find that the terms in ϵ vanish if

$$2a_2(\theta-1)\,(b_2\gamma - b_1c_2h''^2)^2 = 3b_1b_2^2\theta(1-h''^2)\,[(b_2\gamma - b_1c_2h''^2) - 2b_1c_2(1-h''^2)]. \tag{2.23}$$

The strongly superconducting state is in equilibrium with the normal state when the weakly superconducting state is thermodynamically unstable only if the phase diagram has the appearance of figure 2. This requires that $(\theta-1)/\theta$ be positive. It follows from (2.23) that $(\theta-1)/\theta$ has the sign of $(b_2\gamma - 2b_1c_2 + b_1c_2h''^2)$. The least value of this expression corresponds to the least value of the physically significant root of (2.13), which is given by (2.19). Substituting this value, we find that this last expression has a least value of $(b_2\gamma - b_1c_2)\,(2b_1c_2 - b_2\gamma)/b_1c_2$, which is positive on account of the inequalities (2.18). We deduce that a hypo-critical point, at which the second order transition between the normal and the weakly superconducting state gives way abruptly to a first order transition between the normal and the strongly superconducting state, should be experimentally realizable. We assume that transitions between the weakly and the strongly superconducting states will occur without observable hysteresis, since the phase of ψ is already established.

We may investigate the slope θ of the first order transition curve at the hypo-critical point by rewriting (2.23) in the form

$$(\theta-1)/\theta = (3b_2^2/2a_2c_2)\,(z-2z^2), \tag{2.24}$$

where

$$z = b_1c_2(1-h''^2)/(b_2\gamma - b_1c_2h''^2). \tag{2.25}$$

As h''^2 increases from the minimum to the maximum value allowed by (2.19), z decreases from $1-b_1c_2/b_2\gamma$ to 0. The function $(\theta-1)/\theta$ has its greatest value, and so θ has its greatest value, when $z = \frac{1}{4}$. Since h''^2 must satisfy (2.13), this greatest value will only be achieved if D has the particular value $32c_2(b_2\gamma - b_1c_2)/27b_2^2$. The greatest possible slope θ_m is given by

$$(\theta_m - 1)/\theta_m = 3b_2^2/16a_2c_2,$$

which is the same equation as that determining the slope of the first order curve at a Landau critical point. A slope of less than $\theta_m = 1.32$ will indicate that the branch point is of hypo-critical rather than of Landau type.

3. Comparison with experiment

We compare the predictions of this theory first with established experimental data, and then with the results of B.N.M.S.

Tunnelling experiments might be expected to give direct evidence of the existence of a hypo-critical point. The most detailed experiments seem to be those of Douglass (1961), who studied thin films of aluminium in tangential magnetic fields at various temperatures. For films of thickness $\lambda = 300$ nm and less he observed, in the available range of temperatures, only second order transitions, the energy gap tending continuously to zero as the magnetic field was increased. For a film 400 nm thick he observed only first order transitions, the value of $\Delta^2(H_c)/\Delta^2(H \simeq 0)$ decreasing from 0.8 at $t = 0.749$ to about 0.18 at $t = 0.965$. The theory for a thin foil is not different in essence from that for a thin rod (i.e. a_2, b_2 and c_2 have the same signs), and Douglass fitted his points to a curve appropriate to a Landau critical point, with $\Delta^2(H)$ falling rapidly to zero as the temperature is increased to the value at which $d/\lambda(T) = \sqrt{5}$. Douglass assumed $\lambda_{00} = 50$ nm, so $d/2\lambda_{00} \simeq 4$. For whisker no. 21 of B.N.M.S., $r/\lambda_{00} \simeq 10$, and this whisker has $C \leqslant 0$. If we assume that the quantity c_1/b_1 has about the same (negative) value for aluminium as it appears to have for tin, Douglass's thickest foil should probably lie within the region of hypo-critical points. The energy gap when h and δt are just above their values at the hypo-critical point should then be small and finite. The experimental points in the plot of $\Delta^2(H_c)/\Delta^2(H = 0)$ against d/λ should then continue along a line of roughly constant slope until λ becomes somewhat greater than $\sqrt{5}\,d$, and should then fall abruptly to $\Delta^2 = 0$. The observations fit such an interpretation quite as well as they do Douglass's theoretical curve for a Landau critical point, but they do not go to small enough values of Δ^2 to be decisive.

In the course of a long series of observations of the magnetic transition in thin films and foils, Miller & Cody (1968) observed the transitions of 'thick films' in magnetic fields parallel to the films. They expressed their results in terms of the ratio of the field $H_\parallel$ at which hysteresis was first observed to the critical field H_c of a bulk sample at the same temperature, scaling H_c by the factor $T_{c,\,\text{sample}}/T_{c,\,\text{bulk}}$. Ginzburg–Landau theory predicts a change from a second order to a first order transition at $H_\parallel/H_c = 2.2$. The observed critical values of $H_\parallel/H_c$ were in the range 1.4–1.8. Since the ratio of the critical field of a thin sample to that of the bulk material is an increasing function of temperature, this implies that Miller and Cody observed the onset of hysteresis at lower temperatures and higher fields than those predicted by the Ginzburg–Landau theory, which contradicts our interpretation that the onset of a first order transition occurs at lower fields than that of the Landau critical point. Miller & Cody say: 'Whether this is a real deviation from theory or a lack of sensitivity is not clear.' Their films were polycrystalline and probably inhomogeneously strained, with thermal transitions of 'about 10–15 mK', and this may well have delayed the onset of hysteresis. The total transition width for the samples of B.N.M.S., when unstrained, was 2.5–4 mK.

In comparing the predictions of this theory with the observations of B.N.M.S., we note that according to (2.22) we have

$$\theta = \frac{\mathrm{d}h^2}{\mathrm{d}(\delta t)} = \frac{\mathrm{d}(H/H')^2}{\mathrm{d}[(T_c-T)/(T_c-T')]} = \frac{\mathrm{d}(H/H'')^2}{\mathrm{d}[(T_c-T)/(T_c-T'')]}, \tag{3.1}$$

since $H'^2/(T_c-T') = H''^2/(T_c-T'')$. The slope of the thermodynamic equilibrium curve in the first order region is thus unaltered if H and T are normalized with respect to H'' and T'' at a hypo-critical point rather than with respect to H' and T' at a Landau critical point. The prediction of the theory is that for a sample of such a size that $C > 0$ at the Landau critical point, the observed transition occurs at a Landau point with $\theta = 1$. For a rather smaller sample, for which C would be slightly negative at the Landau point, the observed transition is a hypo-critical point with $(H'', T'') \simeq (H', T')$ and $\theta \simeq 1.32$. For still smaller samples there is a hypo-critical point with lower values of H'' and θ. The experiments show, for whisker no. 21 unstrained, $\theta = 1.28$, for whisker no. 21 at maximum strain, $\theta = 1.31$, and for whisker no. P3 at 0.35 % strain, $\theta = 1.63$, with estimated errors of ± 0.1 for no. 21 and ± 0.2 for no. P3. These two whiskers were of roughly the same diameter. If the present theory is applicable, this diameter must be such that a hypo-critical point occurs rather close to the expected position of the Landau critical point. Measurements on whiskers of other diameters are technically difficult: thicker whiskers grown by the 'squeeze' method tend to have very irregular cross sections and to give blurred transitions, while thinner whiskers become very difficult to mount in the straining device. It seems a curious and worrying coincidence that the only observations which are available should show that $C \simeq 0$ at the Landau critical point which is defined by $A = 0$ and $B = 0$.

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