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THE MAGNETIC TRANSITION IN MODERATELY SMALL SUPERCONDUCTORS, AND THE INFLUENCE OF ELASTIC STRAIN

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CONTENTS

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Measurements have been made of the onset of the superconducting phase transition of tin whiskers (single crystals of diameter 1–2 μm and length several millimetres) as a function of temperature T, magnetic field H, and elastic strain ϵ up to 2 %. For samples of this size (denoted 'moderately small' since they are larger than $\lambda(0)$), there is a range of temperatures, approximately 20–30 mK below the transition temperature $T_c(\epsilon)$, for which the transition is of second order in the Ehrenfest sense. Below the temperature denoted $T'(\epsilon)$ the transition is of first order and may exhibit hysteresis.

The phase diagram at constant strain is derived from the equation

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

where ΔG is the free energy difference between the superconducting and normal states, ψ is the wave function of the superconducting electrons, and the coefficients A, B and C each comprise two terms, of which one is field-dependent, being proportional to H^2. The other, field-independent, term is Ginzburg's (1958) expression for the zero-field energy difference, so that A contains a term proportional to $(T_c - T)$, and B is independent of T. Coefficient C contains a field-independent term, assumed independent of T, which we introduce for consistency. The condition $A = 0$ describes both the second-order transition and limiting supercooling, while the transition at thermodynamic equilibrium in the first order region and limiting superheating are described by $B^2 = -\frac{16}{3}AC$ and $B^2 = -4AC$ respectively. The Landau critical point (H', T') is given by $B = 0$, $A = 0$. If the limiting metastable transitions for a cylinder in parallel field are included on a phase diagram, then the supercooling curve is a continuation of the second order curve while the curve for thermodynamic equilibrium branches from it tangentially if $C(H', T') > 0$, or at a slope which is 1.32 times greater than this if $C(H', T') = 0$. The case $C(H', T') < 0$ is discussed elsewhere (Nabarro & Bibby 1974, following paper in this volume). The last case arises because our observations indicate that the field-independent term in C is negative. Estimates of the sample size were made by using the present theory and were in fair agreement with estimates made electron-microscopically.

Expressions for the change at the superconducting transition of the specific heat and other second derivatives of the Gibbs free energy above and below T' are derived.

It is shown theoretically that the transition remains of second order when the sample is strained elastically. Some of the Ehrenfest relations describing a second order transition with two independent variables are experimentally verified from our data.

1. Introduction

The transition of a bulk superconductor to the normal state in the absence of a magnetic field is, except in an immeasurably small range of temperatures (*ca.* 10^{-14} K) close to the critical temperature T_c (Kadanoff *et al.* 1967), of second order in the sense of Ehrenfest (1933). (See also Pippard 1960.) In the presence of a magnetic field the transition is of first order, and may be hysteretic, showing superheating, supercooling or both. If the sample has a dimension small in comparison with the penetration depth of a magnetic field at the temperature of the transition, the penetration of the field can reduce the order parameter ψ continuously to zero, and the transition can be of second order even in the presence of a field (Silin 1951; Ginzburg 1958). The corresponding vanishing of the energy gap has been observed directly by tunnelling experiments (Douglass 1961).

Since the penetration depth $\lambda(T)$ increases to infinity as the temperature T tends to T_c, there exists for a sample of moderate or large size a temperature T' at which $\lambda(T)$ is comparable with its smallest dimension. Transitions occurring at the corresponding field H', or in lower fields, are of second order. On this model, T' does not exist if the sample is so small that its smallest dimension is less than $\lambda(0)$. We call a sample 'moderately small' if its smallest dimension exceeds the penetration depth at zero temperature $\lambda(0)$ but is still small enough for the temperature range between T' and T_c to be experimentally accessible. Pippard (1952) discussed the thermodynamic properties of a sample in this region, at a time when there were no complete theories of superconductivity. Bardeen (1962) showed that even for a 'very' small sample, with a smallest dimension less than both $\lambda(0)$ and the coherence length $\xi(0)$ at zero temperature, the B.C.S. theory leads to a finite value of T'.

The aim of the first part of this paper is to bring together and extend the existing theories, and in particular to relate the thermodynamic properties immediately below T' to those above T'. Our analysis is based on the observation (see, for example, Goldman 1973) that a theory based on series expansions in powers of ψ up to ψ^4 is adequate to describe the transition completely at temperatures above T'. We note that consistent use of terms in ψ^6 is necessary in order to describe the first order transition immediately below T'. While many other examples of Landau critical points such as T' are known (see, for example, Griffiths 1973), this is probably the only example in which the transition of higher order is truly of second order in the Ehrenfest sense, and accurately represented by a theory of the Landau type.

We also present some new experimental results. Our own samples were whiskers of tin, which could be strained elastically by 1 or 2%. Their transition from the superconducting to the normal state in small magnetic fields is a second order transition with two degrees of freedom (strain ϵ and field H) and therefore provides some direct demonstrations of the Ehrenfest equations with two degrees of freedom. These are described in the second part of the paper. (A similar transition surface has been proposed by Hake (1968, 1969), namely that of a type II superconductor at the second critical field H_{c2} at a pressure P, but the mixed state is not a classical homogeneous phase; this surface has not yet been studied experimentally.) If pressure P or stress σ is included as a parameter then instead of a Landau critical point we have a Landau critical line in three dimensional phase space.

I. SAMPLES FREE FROM STRESS

2. Form of the Gibbs free energy

In order that we may later be able to generalize the form of the Gibbs free energy per unit volume, G, we write, following Ginzburg (1958),

$$G = G^s - G^n = -a_1\psi^2 + \tfrac{1}{2}b_1\psi^4 - \tfrac{1}{2}\mu H \tag{2.1}$$

and

$$a_1 = a(T_c - T)/T_c, \tag{2.2}$$

where a and b_1 are positive constants, assumed independent of field H or temperature T. The superscripts s and n denote the superconducting and normal states respectively and $\mu = \int M\,dv$ is the magnetic moment of the sample of volume v. We are concerned with samples so small that the superconducting wave function ψ is uniform, and may therefore take ψ to be real. In zero field, because of (2.2), ψ decreases steadily to zero as the temperature is increased to T_c; in this way a second order transition is described.

In Ginzburg's (1958) normalization, which we use later in this paper (§5), the zero-field equilibrium value ψ_{00} of the order parameter is found by putting $\partial G/\partial\psi = 0$ and is given by

$$\psi_{00}^2 = a_1/b_1, \tag{2.3}$$

leading to

$$G^n - G^s = H_{c,b}^2/8\pi = a_1^2/2b_1, \tag{2.4}$$

where $H_{c,b}(T)$ is the critical field of a bulk sample.

Von Laue's (1949) expression for the magnetization of a cylinder of radius r in a magnetic field H parallel to its axis is

$$M = \mu/v = [-I_2(r/\lambda)\,H]/[4\pi I_0(r/\lambda)], \tag{2.5}$$

where $I_n(x) = \mathrm{i}^{-n}J_n(\mathrm{i}x)$ and J_n is the Bessel function. In this expression, the penetration depth λ is a function of temperature. In the present case, where we assume that $r \ll \xi(T)$, λ is also a function of the applied field H, but it is uniform throughout the sample. In Ginzburg–Landau theory, for a clean material,

$$\lambda^{-2} = 4\pi(e^*)^2\,\psi^2/mc^2 = l_1\psi^2, \tag{2.6}$$

where e^* is twice the electronic charge, m is the effective mass of the carriers, and c is the speed of light. Thus we can expand the right hand side of (2.5) to sixth order in λ^{-1} or ψ to give

$$G = -a_1\psi^2 + \tfrac{1}{2}b_1\psi^4 + m_1H^2\lambda^{-2} - m_2H^2\lambda^{-4} + m_3H^2\lambda^{-6}, \tag{2.7}$$

where

$$m_1 = r^2/64\pi, \quad m_2 = r^4/384\pi \quad \text{and} \quad m_3 = 11r^6/24576\pi. \tag{2.8}$$

For a circular cylinder in transverse field, von Laue's (1949) expression for μ/v is twice that in (2.5), so that m_1, m_2 and m_3 are twice as large as in (2.8).

For consistency we introduce a term $+\tfrac{1}{3}c_1\psi^6$ in the zero-field free energy. We are concerned in this work with transitions which occur very close to T_c, and therefore neglect the temperature dependence of all coefficients except a_1. (Bardeen (1962), who treats transitions in very small specimens, which occur at temperatures well below T_c, uses the temperature-dependent coefficients of the B.C.S. theory.) We obtain

$$G = -a_1\psi^2 + \tfrac{1}{2}b_1\psi^4 + \tfrac{1}{3}c_1\psi^6 + H^2(m_1l_1\psi^2 - m_2l_1^2\psi^4 + m_3l_1^3\psi^6), \tag{2.9}$$

which is of the form

$$G = -A\psi^2 + \tfrac{1}{2}B\psi^4 + \tfrac{1}{3}C\psi^6, \tag{2.10}$$

where

$$A = a_1 - a_2H^2, \quad B = b_1 - b_2H^2 \quad \text{and} \quad C = c_1 + c_2H^2 \tag{2.11}$$

and

$$a_2 = m_1l_1, \quad b_2 = 2m_2l_1^2 \quad \text{and} \quad c_2 = 3m_3l_1^3. \tag{2.12}$$

The coefficients a_1, a_2, b_1, b_2 and c_2 are all positive, while a_1 is a function of T. The equations $A = 0$, $B = 0$ therefore define a singular point, the Landau critical point (T', H'), which is frequently described as a tricritical point. According to Brandt (1973), c_1 is negative, and the behaviour of the sample therefore depends on the sign of $c_1 + c_2H'^2$. Since c_1 is independent of the radius of the sample, while c_2 is proportional to r^6, C will be positive at the Landau critical point for rather large samples and negative for rather small samples. It seems that the only samples for which we have detailed measurements may be of such a size that $C \simeq 0$ at the Landau critical point. We shall also consider the theory for this special case, although our solution will not always be stable against perturbations.

In transverse field, G is of the same form as (2.10), with appropriate values in (2.8).

In the appendix we give formulae analogous to (2.6)–(2.12) in the case of a very small, 'dirty', superconductor, discussed by Bardeen (1962). These formulae are in terms of Δ (the temperature-dependent energy gap) instead of ψ, but both Δ and ψ are implicit variables, so that it is sufficient to show that G has the same form in both cases. Some of the formulae for the various critical fields and temperatures, latent heats and specific heats which are developed in the body of the paper in the Ginzburg limit for 'clean' materials near T_c can be taken over and applied in the Bardeen limit for a very small 'dirty' sample at all temperatures below T_c. In the Bardeen limit λ^{-2} must be expanded in higher powers of Δ^2, while in the Ginzburg limit λ^{-2} is simply proportional to ψ^2. In the Bardeen limit $r \ll \lambda(0)$, so no terms higher than $(r/\lambda)^2$ in $\frac{1}{2}\mu H$ need to be considered. The point T' given by the Bardeen theory is not size-dependent but depends on the parameters $N(0)$ and V of the microscopic theory; Bardeen's formulae were validly used for our whiskers near T_c (Rothberg, Nabarro & McLachlan 1974) but cannot be used to discuss the experimentally observed branch point (H', T'), for which the theory of Ginzburg's type discussed below is used.

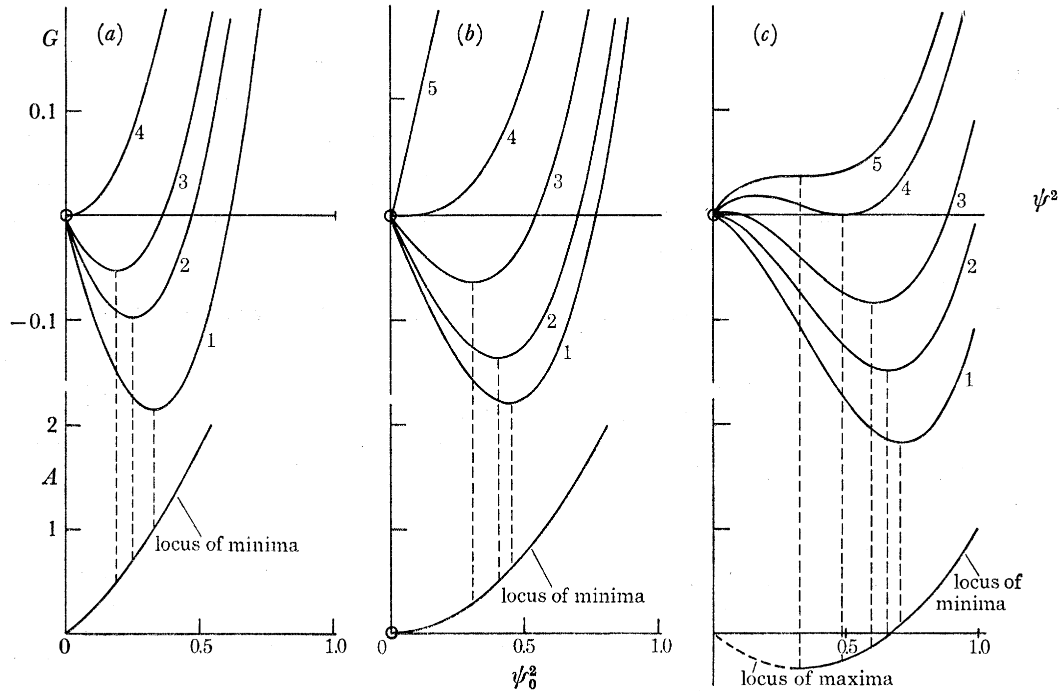

FIGURE 1. Upper axes show the Gibbs free energy G as a function of the order parameter ψ^2, according to (2.10), for $C > 0$ and various values of A. (a) $B > 0$; second order transition for $A = 0$; (b) $B = 0$; Landau critical point for $A = 0$; (c) $B < 0$; first order transitions: limit of supercooling when $A = 0$ (curve 2); thermodynamic equilibrium when $B^2 = -\frac{16}{3}AC$ (curve 4); limit of superheating when $B^2 = -4AC$ (curve 5). Lower axes show the relation between A and the minima ψ_0^2, given by (3.1). When the transition is of first order, ψ_0^2 no longer goes continuously to zero as A becomes zero. Since $A = [a(T_c - T)/T_c] - a_2 H^2$, with a, T_c, a_2 constants, these graphs can be used to describe the nature of the transition as a function of magnetic field H and temperature T. In (a), $C = 3$; $B = 2$; $A = 1$, 0.7, 0.5, 0 for curves 1–4 respectively. In (b), $C = 3$; $B = 0$; $A = 0.6$, 0.5, 0.3, 0, -1 for curves 1–5 respectively. In (c), $C = 3$; $B = -2$; $A = 0.1$, 0, -0.1, -0.25, -0.33 for curves 1–5 respectively.

3. G AS A FUNCTION OF A, B AND ψ

We now exploit the fact that many of the results obtained by Ginzburg (1958), using the exact expression (2.5), can be derived by using terms only up to order ψ^6, so that the simpler equation (2.10) can be used to give analytical results in further discussions, assuming for the present that $C > 0$. We note, however, that it is inconsistent to consider the term $\frac{1}{3}c_2 H^2\psi^6$ while neglecting the term $\frac{1}{3}c_1\psi^6$. The condition $(\partial G/\partial\psi)_{\psi_0} = 0$, applied to (2.10), gives either $\psi_0 = 0$ (the normal state) or

$$\psi_0^2 = [-B \pm \sqrt{(B^2 + 4AC)}]/2C. \tag{3.1}$$

We use the convention that the radical denotes the positive square root. If the positive sign is chosen and if either A or C is small then (3.1) tends to

$$\psi_0^2 = A/B, \tag{3.2}$$

which is the solution that is obtained by putting $C = 0$ in (2.10).

The sketches on the upper axes of figures 1 *a*, *b*, and *c* show G as a function of ψ^2. C is positive in all three cases, but B is positive, zero and negative in figures 1 *a–c* respectively. The value of A decreases to give curves 1, 2, 3, 4 and 5 on each graph. On these graphs the minima ψ_0^2 are found by taking the positive sign of the radical in (3.1), while the maxima in figure 1 *c* are obtained by taking the negative sign. The relation between ψ_0^2 and $A = [a(T_c - T)/T_c] - a_2H^2$ is plotted in the lower parts of the figures with the same abscissa scale.

In figures 1 *a*, *b*, ψ_0^2 decreases continuously to zero as A is decreased, and the transition is of second order, occurring at $A = 0$. In figure 1 *b*, the lower graph has a horizontal slope at $A = 0$; this series of three figures shows that the change from second to first order transitions occurs when $B = 0$. This can be seen analytically from (3.2), since real solutions for ψ^2 are only obtained if $B > 0$ when $A = 0$. Thus ($A = 0$, $B = 0$) gives the Landau critical point, namely the lowest temperature T' and highest field H' at which the transition is still of second order.

Table 1. Values of A, B and ψ_0^2 at the superconducting transition, for $C > 0$

	type of transition	equations determining the transition	value of ψ_0^2	relation between A, B, and C
second order region	thermodynamic equilibrium transition	$dG/d\psi^2 = 0$ $\psi_0 = 0$	0	$A = 0$ $B > 0$
first order region	limit of super-cooling	$dG/d\psi^2 = 0$ $\psi_0 = 0$	$-B/C$	$A = 0$ $B < 0$
	thermodynamic equilibrium transition	$dG/d\psi^2 = 0$ $G = 0$ $\psi_0 \neq 0$	$-3B/4C$	$A < 0$ $B^2 = -16AC/3$
	limit of superheating	$d^2G/(d\psi^2)^2 = 0$ $dG/d\psi^2 = 0$ $\psi_0 \neq 0$	$-B/2C$	$A < 0$ $B^2 = -4AC$

In figure 1 *c* the value $A = 0$ (curve 2) no longer corresponds to a transition to the normal state. As A is decreased further, $G(\psi^2)$ develops a maximum, which forms a potential barrier so that in curve 4, although simultaneously $G = 0$ and $dG/d\psi = 0$ both for $\psi = 0$ and for $\psi_0 \neq 0$, the transition between these equilibrium states is hindered. As A is reduced further, a metastable state persists until the maximum and minimum coincide in curve 5 and the metastable state disappears, when the sample becomes normal; as is seen in the lower diagram, ψ_0^2 drops suddenly to zero: the transition is of first order. Curves 2 and 5 correspond to first order transitions at the limits of supercooling and superheating, while curve 4 corresponds to thermodynamic equilibrium between the superconducting and normal states. Criteria for the various critical conditions were stated by Ginzburg (1958) and are shown in table 1. The condition $C = 0$ does not give rise to any phase boundaries.

The criterion $A = 0$, $B > 0$ for the transition in the second order region is independent of C and the transition curve is given by

$$a(T_c - T)/T_c = a_2H^2. \tag{3.3}$$

In the Ginzburg limit where $a_1 = m_1 l_1 H^2$ the transition curve is given (using (2.3), (2.4) and (2.6)), by

$$H_c^2(T) = 16\lambda_0^2(T)\, H_{c,b}^2/r^2; \tag{3.4}$$

here $\lambda_0(T)$ is the zero-field penetration depth and $H_c(T)$ is the enhanced critical field of a small sample.

To analyse our data, we use the experimentally determined (Mapother 1962; Daunt *et al.* 1948) explicit dependences on the reduced temperature $t = T/T_c$

$$H_{c,b} = H_{00}(1-t^2) \simeq 2H_{00}(1-t) \quad \text{if} \quad T \simeq T_c \tag{3.5}$$

and

$$\lambda_0(T) = \lambda_{00}(1-t^4)^{-\frac{1}{2}} \simeq \lambda_{00}(1-t)^{-\frac{1}{2}}/2 \quad \text{if} \quad T \simeq T_c, \tag{3.6}$$

where H_{00} and λ_{00} denote values at absolute zero, as in Ginzburg (1958). The transition curve is thus given by

$$H_c^2 = 16(\lambda_{00}/r)^2 H_{00}^2 (T_c - T)/T_c, \tag{3.7}$$

so that a graph of H_c^2 against T has a slope of

$$(\partial H_c^2/\partial T) = -16(\lambda_{00}/r)^2 H_{00}^2/T_c. \tag{3.8}$$

In transverse field, the second order transition is given by the same condition $A = 0$, but m_1, m_2 and m_3 are twice as large, so $(\partial H_c^2/\partial T)$ has half the value of (3.8). Lutes (1957) used a similar analysis, verifying that H_c^2 was proportional to T in the second order region near T_c, for six whiskers. Our experimental results are new in that, as will be discussed in the second part of the paper, elastic strain ϵ_i is an experimental parameter which we could control, while Lutes's whiskers were strained to a constant but unknown extent.

The Landau critical point (T', H') is given by $A = 0$, $B = 0$. In the Ginzburg limit this gives

$$\lambda(T') = r/\surd 3 \tag{3.9}$$

and

$$H' = 4H_{c,b}(T')/\surd 3. \tag{3.10}$$

In the second order region, $r \leqslant \surd 3\lambda(T)$. The same conditions (3.9) and (3.10) are obtained in transverse field.

4. G as a function of H and T

The value of G in a state of equilibrium is obtained by substituting into (2.10) the value of ψ_0^2 given by (3.1), where A, B and C are given, as functions of the radius and material of the specimen and of H and T by (2.11), (2.12), (2.6), (2.7) and (2.8). The nature of the sample is specified by the three quantities H_{00}, T_c and r/λ_{00}, and it is convenient to normalize the expression for G in terms of the values of H and T at the Landau critical point, namely (H', T').

The equations $A = 0$, $B = 0$, which define the Landau critical point, give

$$H' = (b_1/b_2)^{\frac{1}{2}} \tag{4.1}$$

and

$$T' = T_c - a_2 b_1 T_c/b_2 a. \tag{4.2}$$

We define

$$h = H/H' \tag{4.3}$$

and

$$\delta t = (T_c - T)/(T_c - T'). \tag{4.4}$$

The equation $(A = 0)$ of the transition curve in the second order region is then

$$h^2 = \delta t. \tag{4.5}$$

The same equation gives the normalized supercooling field $h_{s.c.}$ in the first order region. This is to be expected, since the second order transition and the first order transition from the normal to the superconducting state on supercooling both occur when a zero of $\partial G/\partial\psi$ occurs infinitesimally close to the zero which is always present at $\psi = 0$. The normalized thermodynamic field h_T and the normalized superheating field $h_{\mathrm{s.h.}}$ in the first order region are given by

$$(1-h_T^2)^2 = -\frac{16a_2}{3b_2}(\delta t - h_T^2)\left(\frac{c_1}{b_1}+\frac{c_2}{b_2}h_T^2\right) \tag{4.6}$$

and

$$(1-h_{\mathrm{s.h.}}^2)^2 = -\frac{4a_2}{b_2}(\delta t - h_{\mathrm{s.h.}}^2)\left(\frac{c_1}{b_1}+\frac{c_2}{b_2}h_{\mathrm{s.h.}}^2\right), \tag{4.7}$$

where, from (2.8) and (2.12), the product

$$a_2c_2/b_2^2 \simeq 0.7734. \tag{4.8}$$

This is the first time in our analysis that the coefficient C of the sixth order term in ψ plays a part. This is to be expected. In the neighbourhood of the second order equilibrium line we are concerned with a minimum of the function $G(\psi^2)$ which occurs for small values of ψ^2. The term $\frac{1}{3}C\psi^6$ in (2.10) is then negligibly small. If $C > 0$, the curves have the forms sketched in figures 1 *a*, *b*; if $C < 0$, and we terminate the series for G with the term in ψ^6, $G(\psi^2)$ decreases without limit as ψ^2 tends to infinity, but this unphysical region is separated from the region of small ψ^2 in which we are interested by a maximum of $G(\psi^2)$. In the first order region we are concerned with a minimum of $G(\psi^2)$ which occurs for a finite value of ψ^2 when $C > 0$, and does not occur when $C < 0$ unless (2.10) is supplemented by terms of higher order in ψ^2.

We first assume that C is non-negative at the Landau critical point, so that

$$b_1c_2+b_2c_1 \geqslant 0. \tag{4.9}$$

Since the same equation (4.5) describes both the second order thermodynamic equilibrium curve and the supercooling curve, these two loci will be continuous on a plot in $(h^2, \delta t)$ space and the thermodynamic equilibrium curve in the first order region, given by (4.6), will branch from this curve at an angle θ at the Landau critical point ($h^2 = \delta t = 1$). If δt is increased by an infinitesimal amount ϵ, then

$$h^2 = 1+\epsilon\theta \quad \text{and} \quad \delta t = 1+\epsilon, \tag{4.10}$$

and (4.6) gives

$$16a_2\epsilon(1-\theta)(b_1c_2+b_2c_1) = -3b_1b_2^2\epsilon^2\theta^2 - 16a_2b_1c_2\epsilon^2\theta(1-\theta). \tag{4.11}$$

If $C \neq 0$ at the Landau critical point, $b_1c_2+b_2c_1 \neq 0$, and (4.11) is satisfied to first order in ϵ if $\theta = 1$; the thermodynamic equilibrium curve in the first order region is tangential to that in the second order region, at the Landau critical point. If $C = 0$ at the Landau critical point then (4.11) must be taken to second order in ϵ, and $\theta = 1$ is no longer a solution; we obtain

$$\theta/(1-\theta) = -16a_2c_2/3b_2^2 = -4.125. \tag{4.12}$$

Using (4.8), this predicts that, if $C = 0$ at the Landau critical point, the two thermodynamic equilibrium curves must branch from each other, the slope of the second order curve being unity if h^2 is plotted against δt, while the slope of the first order curve is

$$\mathrm{d}(h_T^2)/\mathrm{d}(\delta t) = 1.32, \tag{4.13}$$

or, in non-normalized units,

$$(\mathrm{d}(H^2)/\mathrm{d}T)_{H'T'} = -1.32(H')^2/(T_c - T').$$

We note that if $C(H', T') = 0$, $C > 0$ for $T < T'$. The case in which $C(H', T') < 0$ is discussed in the following paper (Nabarro & Bibby 1974), and gives rise to a singularity which we call a hypo-critical point.

If $C(H', T') > 0$, the qualitative results do not depend on the exact value of c_1, and the curves of figures 2 and 3 are plotted for the Ginzburg–Landau value $c_1 = 0$.

Figure 2 shows h as a function of δt. Below $B = 0$, the curves $B^2 = -4AC$ and $B^2 = -16AC/3$ represent solutions which are not physically realizable, since ψ_0^2 is real but negative; such a solution will occur for instance for curve 5 in figure 1*b*.

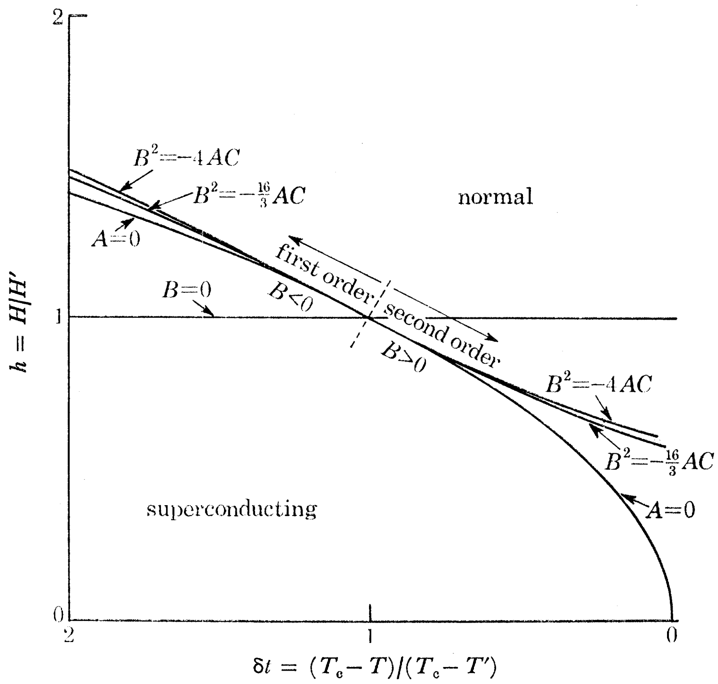

FIGURE 2. Phase diagram for a small superconductor, showing field as a function of temperature where both quantities have been normalized in terms of the coordinates of the Landau critical point ($A = 0$, $B = 0$). Curves are shown for the Ginzburg–Landau value $c_1 = 0$. When $B > 0$, second order transitions occur when $A = 0$. When $B < 0$, the limit of supercooling occurs when $A = 0$, thermodynamic equilibrium when $B^2 = -\frac{16}{3}AC$, and the limit of superheating when $B^2 = -4AC$.

To complete the normalization, we define

$$G' = (H')^2/8\pi \tag{4.14}$$

and

$$g = G/G' = (G^s - G^n)/G'. \tag{4.15}$$

Figures 3*a*, *b* show $(-g)$ as a function of δt for different values of h. Figure 3*b* represents the region near (H', T') on an enlarged scale. At $h = 0$, the graph has a horizontal tangent $\partial g/\partial t = 0$; the latent heat is zero and the transition is of second order. The curvature of the graphs at the points $g = 0$ measures the change in the specific heat $\Delta^{ns}C_H = -T\,\partial^2 G/\partial T^2$ at the transition, which thus is seen to be finite for $T' < T \leqslant T_c$. The curvature of the graphs of $(-g)$ against δt at $g = 0$ in figure 3 is infinite at (T', H'), gradually becoming less as the field is decreased below H'. The tails which curve upwards for $T > T_c(H)$ represent the physically unrealizable solutions for negative ψ_0^2, and terminate at the points where ψ_0^2 becomes complex. These features were predicted by Pippard (1956) on the two-fluid model, and are shown on his figure 2. When $h > h'$, superconducting solutions exist for $g > 0$, implying that $G^s > G^n$. These represent superheating. For these curves, $\partial g/\partial t \neq 0$ at $g = 0$, so there is a latent heat, the transition being of first order.

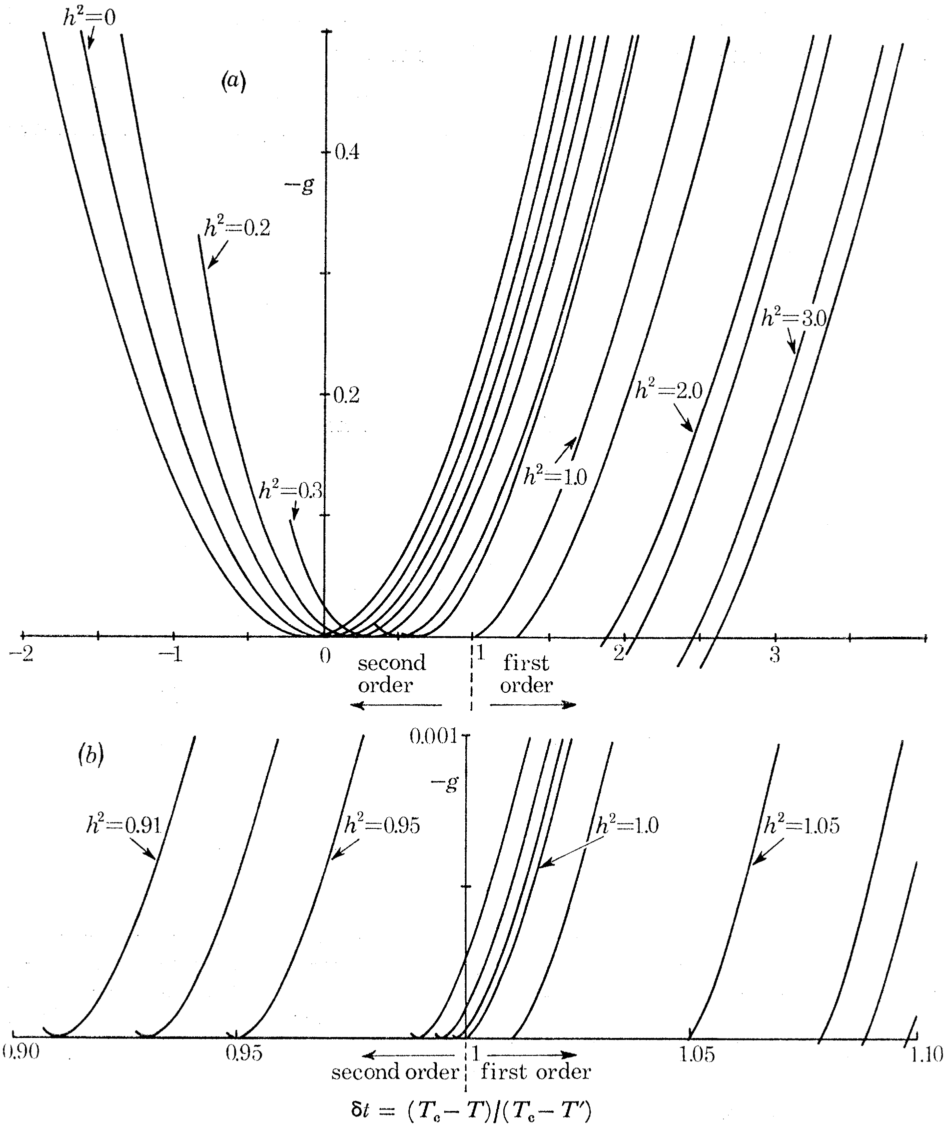

FIGURE 3. Gibbs free energy difference as a function of temperature, at various fields, where these quantities have been normalized in terms of their values at the Landau critical point $h^2 = \delta t = 1$, and where $c_1 = 0$. In (*b*) the scale has been expanded near the Landau critical point. The slope $\partial g/\partial(\delta t)$ at $g = 0$ for any value of h is proportional to the latent heat of the normal–superconducting transition, while the curvature is proportional to the change in the specific heat at the transition. Tails curving upwards to the left represent physically unrealizable solutions for negative ψ_0^2 terminating at points where ψ_0^2 becomes complex. All other solutions are for real and positive ψ_0^2. The tails pointing downwards in the first order region correspond to metastable states.

5. First and second derivatives of G in the neighbourhood of the Landau critical point

The evaluation of the derivatives of G is simplified by the fact that our assumed form depends on T only through A (see (2.11) and (2.2)). It is in practice convenient to use the form (2.10), together with the explicit dependence of ψ_0^2 on H and T given by (3.1). The results for the discontinuity in C_H, the specific heat at constant magnetic field, are summarized in table 2. The results of tables 1 and 2 are essentially those of Landau (1935) and Ginzburg (1958).

There is a singularity at the Landau critical point, where $B = 0$, the discontinuity in specific heat becoming infinite at this point as was predicted by Pippard (1956) for the second order region. This high value of ΔC_H arises from the rapid dependence of ψ_0^2 on T, given by

$$\frac{\partial \psi_0^2}{\partial T} = \frac{\partial A/\partial T}{\sqrt{(B^2+4AC)}}. \tag{5.1}$$

On the second order transition curve we have $A = 0$, $\mathrm{d}A/\mathrm{d}T = \text{constant}$ and $B \propto T-T'$, which leads to $\Delta C_H \propto (T-T')^{-1}$. However, this high value of $\mathrm{d}\psi_0^2/\mathrm{d}T$ is confined to a temperature range in the neighbourhood of the transition curve in which $4AC < B^2$, i.e. a range of temperature of order $(T-T')^2/(T_c-T')$. At constant magnetic field we have

$$0 < \frac{-\partial \psi_0^2}{\partial T} < \frac{-\partial A/\partial T}{\sqrt{(4AC)}} \propto \frac{1}{\sqrt{[T_c(H)-T]}}, \tag{5.2}$$

with a corresponding behaviour of C_H, so that $\int \Delta^{\mathrm{ns}} C_H \,\mathrm{d}T$ converges even when the upper limit is taken on the transition curve.

Our results also show (figure 4) how the specific heat discontinuity at $T_c(H)$ decreases as H is increased above H'. Considering the thermodynamic equilibrium field H_T, we see that ΔC_H has the same form $K/|T-T'|$ on either side of T', the coefficient K increasing by a factor of two

TABLE 2. CHANGE IN FIRST AND SECOND DERIVATIVES OF G WITH RESPECT TO T, AT VARIOUS CRITICAL FIELDS

(L, latent heat; S, entropy; C_H, specific heat at constant field.)

	thermodynamic critical field in second order region, H_T	limit of supercooling field, $H_{\mathrm{s.c.}}$	thermodynamic critical field in first order region, H_T	limit of superheating field, $H_{\mathrm{s.h.}}$
sign of B	+	−	−	−
$\Delta^{\mathrm{ns}}S = \partial G/\partial T = L/T$	0	$\frac{B}{C}\frac{\partial A}{\partial T}$	$\frac{3B}{4C}\frac{\partial A}{\partial T}$	$\frac{B}{2C}\frac{\partial A}{\partial T}$
$\frac{\partial^2 G}{\partial T^2} = \frac{\Delta^{\mathrm{ns}}C_H}{T}$	$\frac{-1}{B}\left(\frac{\partial A}{\partial T}\right)^2$	$\frac{1}{B}\left(\frac{\partial A}{\partial T}\right)^2$	$\frac{2}{B}\left(\frac{\partial A}{\partial T}\right)^2$	∞

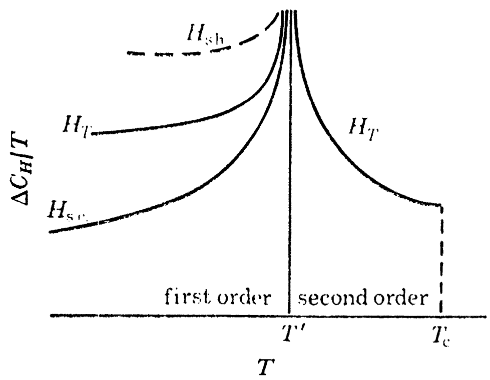

FIGURE 4. Discontinuity in the specific heat at the superconducting–normal transition, as a function of temperature. In the second order region, the discontinuity at the thermodynamic critical field $H_T(T)$ is finite, increasing as the temperature T is reduced, to become infinite at $H_T(T')$. In the first order region the magnitude of the specific heat discontinuity depends on whether the transition occurs at the supercooling field $H_{\mathrm{s.c.}}(T)$, at the thermodynamic field $H_T(T)$ or at the superheating field $H_{\mathrm{s.h.}}(T)$. In the last case the discontinuity is infinite.

when the transition changes from second to first order. We do not know how far below T' our formulae for the first order region are valid, but expect them to be useful down to about $2T'-T_c$.

In the second order region we can write (using (3.5), (2.2), (2.3) and (2.4))

$$\Delta^{\mathrm{ns}} C_H = TH_{c0}^2/\pi T_c^2(1-\delta t), \tag{5.3}$$

agreeing with the Rutgers relation at $T = T_c$.

We now consider the change at the transition of other second derivatives of G. The magnetic moment M is given, from (2.9), by

$$M = -(\partial G/\partial H)_T = -2H(a_2\psi_0^2 - \tfrac{1}{2}b_2\psi_0^4 + \tfrac{1}{3}c_2\psi_0^6), \tag{5.4}$$

where ψ_0^2 is again given by (3.1). The term in $(\partial G/\partial\psi^2)(\partial\psi^2/\partial H)$ vanishes, because the equilibrium value ψ_0^2 is determined by $\partial g/\partial\psi^2 = 0$ when $\psi = \psi_0$. We find

$$\left(\frac{\partial M}{\partial T}\right)_H = -2H\frac{\partial A}{\partial T}\frac{1}{\sqrt{(B^2+4AC)}}(a_2 - b_2\psi_0^2 + c_2\psi_0^4). \tag{5.5}$$

In the second order region $A = 0$ and $\psi_0^2 = 0$ at the transition, so that

$$\left(\frac{\partial M}{\partial T}\right)_H = \frac{-2Ha_2}{B}\frac{\partial A}{\partial T}, \tag{5.6}$$

which has a singularity at the Landau critical point of the same form as that of the specific heat. In the first order region, $(\partial M/\partial T)_H$ also has the same sort of behaviour as the specific heat discontinuity; for example, in the thermodynamic equilibrium field H_T we find

$$\left(\frac{\partial M}{\partial T}\right)_H = -2H\left(\frac{\partial A}{\partial T}\right)\frac{2}{B}\left(a_2 + \frac{3B}{4C}b_2 + \frac{9B^2}{16C^2}c_2\right). \tag{5.7}$$

The second and third terms are finite and zero respectively at $B = 0$, so that the ratio of $(\partial M/\partial T)_H$ to the discontinuity in the specific heat is constant in the neighbourhood of the Landau critical point.

It can also be shown (from (5.4) and (3.1)) that $(\partial M/\partial H)_T$ has the same behaviour at and near the Landau critical point as have the other two second derivatives of G.

It is to be expected that other second derivatives of G behave in the same way. For example, the discontinuity at the transition of the elastic modulus should become infinite at the Landau critical point. This infinity can be interpreted physically if it is remembered that the change from a second to a first order transition implies a change into a situation where there is a volume change at the transition. Properties of samples under strain are discussed in the second part of this paper.

In view of the results of this section, one may be concerned whether measurements of the discontinuities in various properties at temperatures below T' can be extrapolated through T' to give the values at T_c. This is in fact the experimental procedure adopted, for example, on measuring the change in specific heat at the superconducting transition (Cochran 1962), the change in the coefficient of thermal expansion (White 1964), or the change of elastic modulus (Gibbons & Renton, 1959). All these measurements were made on large samples, for which T' is very close to T_c, so that extrapolations are being made through T' to obtain the value at T_c. The following argument shows that these extrapolations are justified.

Suppose that measurements are made of the change in a given property at the superconducting transition, using a large and a small sample. Results on the two samples at a given temperature below T_c will differ because the large sample excludes the magnetic field while the small sample allows the field to penetrate. At T_c there is no magnetic field, so that the same results must be obtained for both large and small samples. Thus the results obtained on large samples below T' (where there is no field penetration because of their size) must extrapolate continuously to the results at T_c (where there is no field penetration because $H = 0$). The singularity at T' produced by the penetration of the field is superposed on this smoothly extrapolated curve.

Equation (5.6) describing the second order region can be derived directly using terms only as far as ψ^4 in G, since $\psi_0^2 = A/B$, and

$$M = -2H(a_2\psi^2 + \tfrac{1}{2}b_2\psi^4),$$

so that

$$(\partial M/\partial T)_H = -\frac{2Ha_2}{B}\frac{\partial A}{\partial T} + \frac{2Hb_2}{B^2}A\frac{\partial A}{\partial T}; \tag{5.8}$$

the second term is zero along the transition curve. Since $A = 0$ along the transition curve in the second order region we also have

$$(\partial M/\partial H)_T = \frac{-2Ha_2}{B}\frac{\partial A}{\partial H} \tag{5.9}$$

and

$$(\partial M/\partial \sigma)_{H,T} = \frac{-2Ha_2}{B}\frac{\partial A}{\partial \sigma}, \tag{5.10}$$

where σ is the stress applied to the sample. These three second derivatives of G all have the same variation with temperature and field. They differ from ΔC_H in that they are all zero at T_c, as is to be expected since there is then no field to penetrate the sample. They all increase with decreasing temperature in the same way as does ΔC_H, becoming infinite at the Landau critical point. We shall see in the second part of this paper that the Ehrenfest relations require that such interrelations between the second derivatives should hold.

In order to use equations (5.8), (5.9) and (5.10) in part II of the paper, we use Ginzburg's (1958) normalization (see (2.3) and (2.4)) so as to work explicitly in terms of r/λ_{00} and H_{00}, and we also use the explicit temperature dependences of (3.5) and (3.6). These expressions for the derivatives of M with respect to H, T and σ neglect changes with H and T of the volume v and radius r. The quantity B becomes $B = b_1 B'$ where

$$B' = 1 - \tfrac{1}{12}(r/\lambda_{00})^4 (H/H_{00})^2 \tag{5.11}$$

and then

$$\left(\frac{\partial M}{\partial T}\right)_{H,\sigma} = \frac{vH}{8\pi B'}\left(\frac{r}{\lambda_{00}}\right)^2 \frac{1}{T_c}, \tag{5.12}$$

$$\left(\frac{\partial M}{\partial H}\right)_{T,\sigma} = \frac{v}{4\pi B'}\left(\frac{r}{\lambda_{00}}\right)^2\left(1-\frac{T}{T_c}\right), \tag{5.13}$$

$$\left(\frac{\partial M}{\partial \sigma}\right)_{H,T} = \frac{-Hv}{8\pi B'}\left(\frac{r}{\lambda_{00}}\right)^2\left[\left(1-\frac{T}{T_c}\right)\left(\frac{2\,\mathrm{d}\ln H_{00}}{\mathrm{d}\sigma} + \frac{2\,\mathrm{d}\ln(\lambda_{00}/r)}{\mathrm{d}\sigma}\right) + \frac{T}{T_c}\frac{\mathrm{d}\ln T_c}{\mathrm{d}\sigma}\right] \tag{5.14}$$

and from (5.3)

$$\Delta^{ns} C_H = TH_{00}^2/\pi T_c^2 B' = \Delta C(T_c)/B'T_c. \tag{5.15}$$

6. Experimental method and results

The superconducting transitions of tin whiskers at fixed but unknown strains were studied by Lutes & Maxwell (1955) and by Lutes (1957), who found that the size of a typical whisker is such that the transition is of second order over an easily measurable range of temperatures near T_c, typically 30 mK.

Experimental details are given by Rothberg, Nabarro & McLachlan (1971). Sources of error in the absolute strain calibration are re-evaluated here: a total error of $\pm 4.3\,\%$ arises from contributions of $\pm 0.3\,\%$, $\pm 1\,\%$ and $\pm 3\,\%$ from the change with temperature of the elastic modulus of the stainless steel block which determines the strain, the room temperature calibration error, and the whisker gauge length measurement respectively. Despite this fairly large error in absolute strain, uniform increments in strain could be applied with complete reproducibility, except for one case (whisker no. P3) where some backlash was observed and corrected.

The transition temperature T_c was found to increase with strain for all four orientations studied ([001], [100], [110], [111]) so that the sample in the normal state at zero field could be driven superconducting by straining it at a fixed temperature. The error in measurement of T_c is ± 0.5 mK. Our results agree well with those of Davis, Skove & Stilwell (1966) and Cook (1971). For whiskers of [001] orientation, the shift is linear, at a rate of 0.419 ± 0.010 K per 1 % strain, so that

$$\mathrm{d}\ln T_c/\mathrm{d}\epsilon_3 = 11.2 \pm 0.3, \tag{6.1}$$

which corresponds to a shift of

$$\mathrm{d}T_c/\mathrm{d}\sigma_3 = (4.83 \pm 0.12) \times 10^{-11}\ \mathrm{K\,cm^2/dyn} \tag{6.2}$$

(using the compliances at low temperatures of Rayne & Chandrasekhar 1960). For whiskers of [100] orientation, the shift is parabolic.

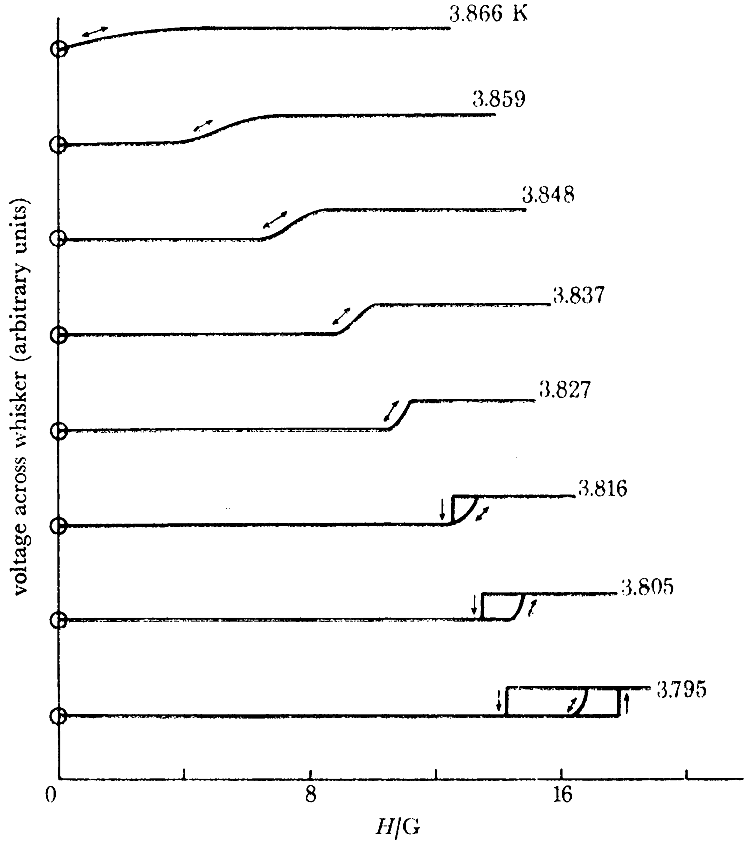

FIGURE 5. Recorder tracings showing the measurement of the critical field $H_c(T, \epsilon)$ at a fixed strain (0.35 %) at gradually reduced temperatures near $T_c(\epsilon)$ for whisker no. P3 of [001] axial orientation. Double-headed arrows indicate a reversible transition; single arrows denote superheating and supercooling which occur when the transition is no longer of second order. (1 G = 10^{-4} T.)

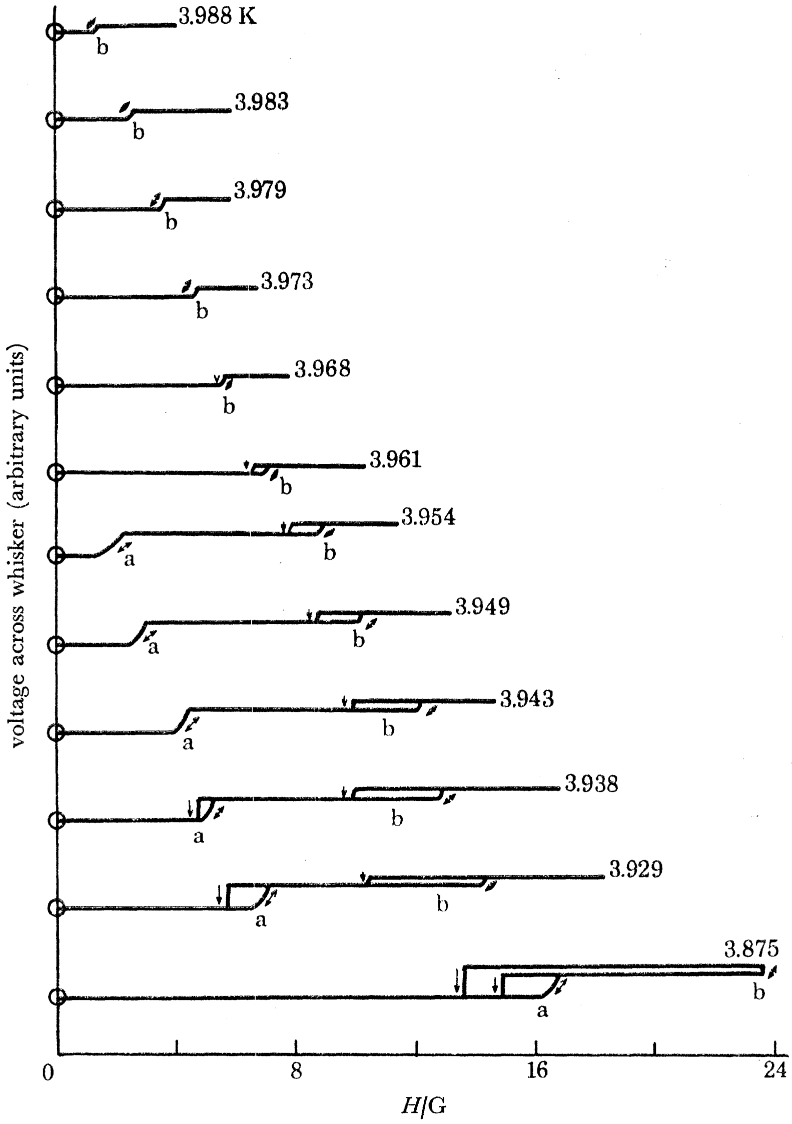

FIGURE 6. Recorder tracings showing measurement of $H_c(T, \epsilon)$ for a [100] whisker, no. 24, which comprised two segments of differing cross sections, hence at differing strains, the voltages across these segments being labelled a and b. (1 G = 10^{-4} T.)

To map out the second order transition surface in (H, T, ϵ) space, the procedure adopted was to set the strain of the sample, measure T_c, and then gradually reduce the temperature, measuring $H_c(T, \epsilon)$ at closely spaced stabilized temperatures (about 5 mK apart). The transition was reversible, its width decreasing with temperature. The critical field $H_c(T, \epsilon)$ was taken as that field at which the voltage across the whisker, produced by a small measuring current, was half the voltage in the normal state. At some temperature the onset of hysteresis, usually supercooling, indicated that the transition was now of first order; at still lower temperatures superheating also often occurred. At this stage the strain of the sample was changed and the procedure repeated. Typical recorder tracings are shown in figure 5 and figure 6. The cross section of the whisker shown in figure 6 apparently changed abruptly at some point down its length so that the two segments, denoted a and b, acted as two whiskers in series carrying the same load and their stress

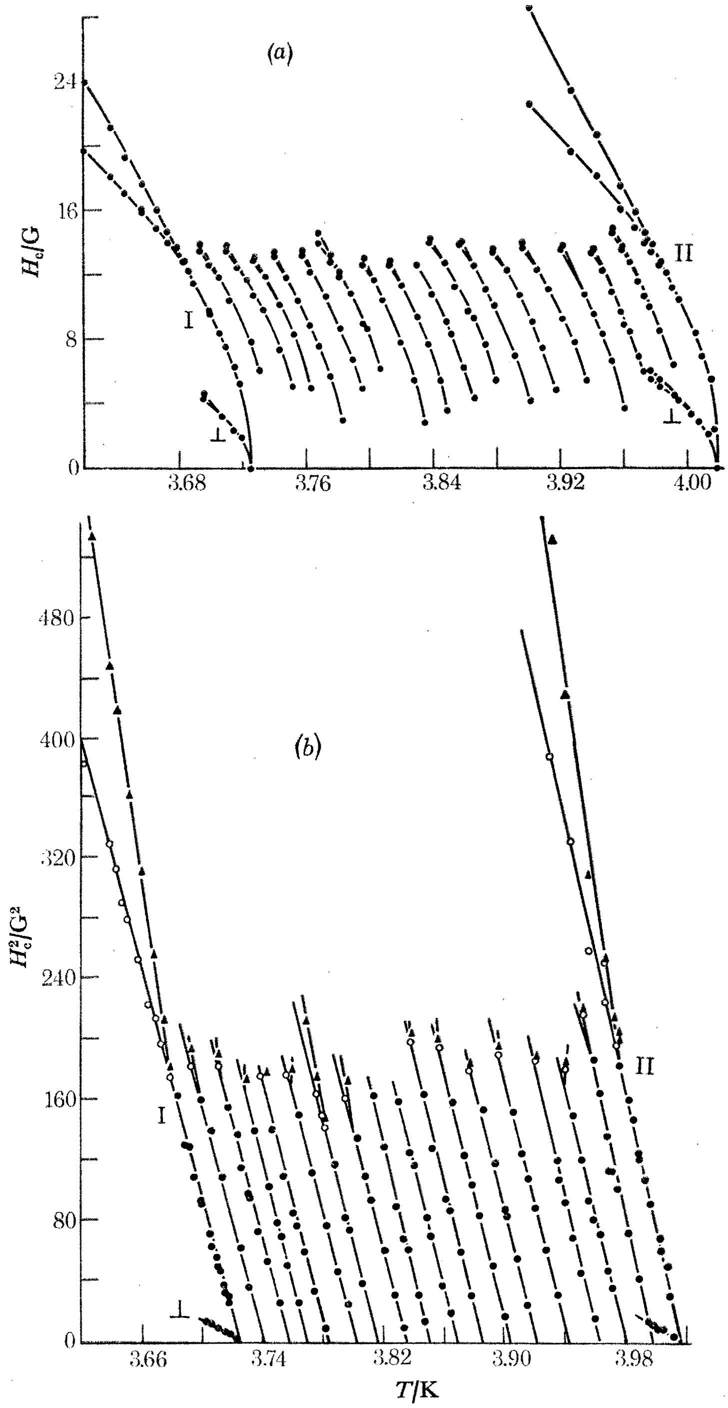

FIGURE 7. Graphs of (*a*) critical field $H_c(T, \epsilon)$ and (*b*) $H_c^2(T, \epsilon)$ as functions of temperature T at various strains ϵ for whisker no. 21, of [001] axial orientation. Successive curves are at strain increments of 0.045 %, the curve I being the zero-strain curve. Some supercooling points are included, appearing as lower branches for $T < T'(\epsilon)$, and some points in transverse field are also shown. In figure 7*b*, the same straight line can be drawn through the supercooling field points and the second order critical field points. (1 G = 10^{-4} T.)

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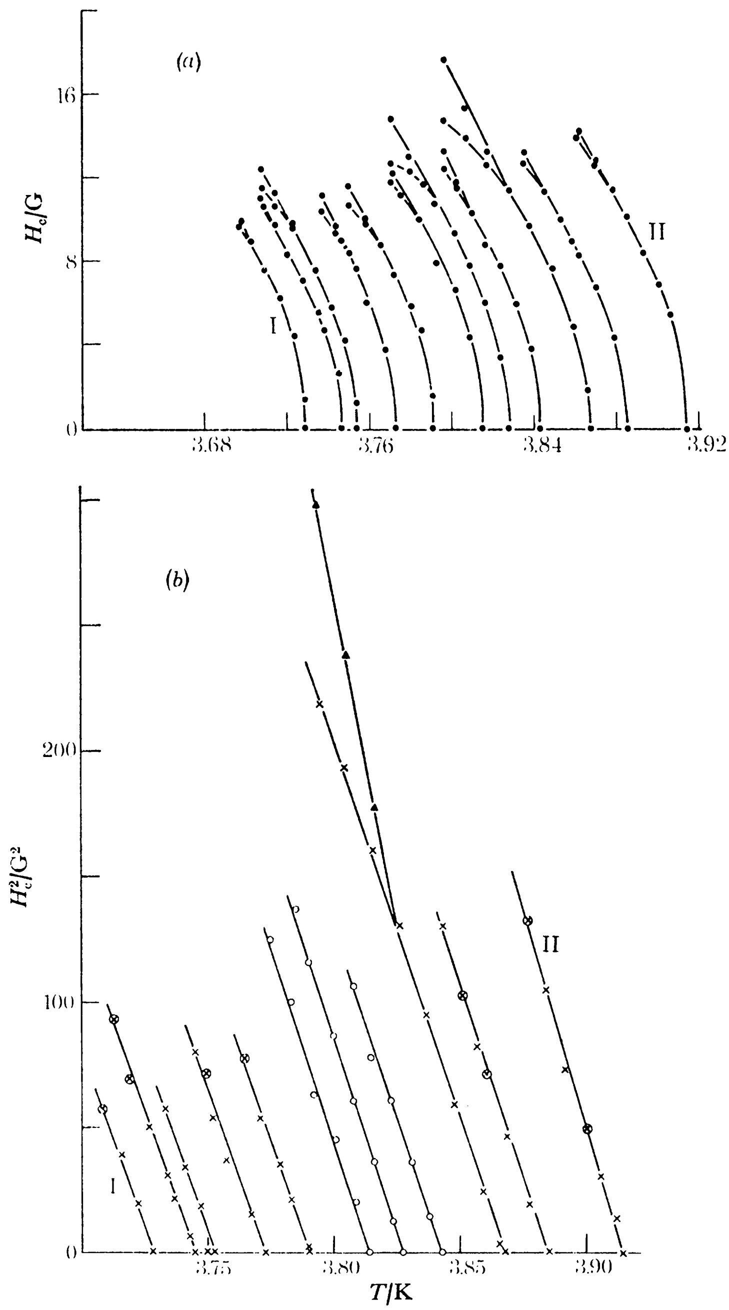

FIGURE 8. Graph of (*a*) critical field $H_c(T, \epsilon)$, (*b*) $H_c^2(T, \epsilon)$ for whisker no. P3 of [001] axial orientation at strain increments of 0.045%. Curve I is the zero-strain curve. (1 G = 10^{-4} T.)

differed; at a given nominal strain of the sample as a whole, the two segments therefore had different values of T_c. Moreover, because of its lower $T_c(\epsilon)$, segment *a* could still be in the second order region at a given temperature while segment *b* was already in the first order region and exhibited hysteresis. The two segments are plotted as separate specimens.

Some measurements were also made in a field perpendicular to the whisker axis, but attention was concentrated on parallel-field behaviour, mainly because the cross section of the whisker was irregular and so a transverse field may be strongly concentrated along ribs at which the

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transition is initiated. Transverse fields may possibly give rise to an intermediate state or even to flux flow in the whisker (see, for example, Rothberg *et al.* 1971). The shapes of the transitions in transverse field were similar to those in parallel field, sometimes being broader.

Figures 7*a*, *b* show $H_c(T, \epsilon)$ and $H_c^2(T, \epsilon)$ as functions of temperature T for a whisker of [001] axial orientation (no. 21) at zero strain (curve I) and at successive strain increments of 0.04 %. Thus curve II is at a strain of 0.67 %. Measurements could not be taken at higher strains because the cryostat could not be pressurized much above atmospheric pressure ($\simeq$ 83 kPa (62 cm Hg) in Johannesburg), setting a maximum temperature of about 4.05 K. Supercooling fields have also been plotted on figure 7*a*, so that the point at which a given curve branches indicates $T'(\epsilon)$; the locus of such points is a boundary of the second order surface. Some results in transverse field are also shown. Similar curves for another [001] whisker (no. P3) are shown in figures 8*a*, *b*. The apparently nonlinear shift of the (H_c, T) curves was due to slight jamming of the straining device, which was subsequently corrected; nominally these curves are also at uniform strain increments, of 0.045 %. The true strain of each curve could be found since $T_c(\epsilon)$ was known. It is seen that $(T_c - T')$ increases with strain for this whisker, although it was fairly constant for the previous one.

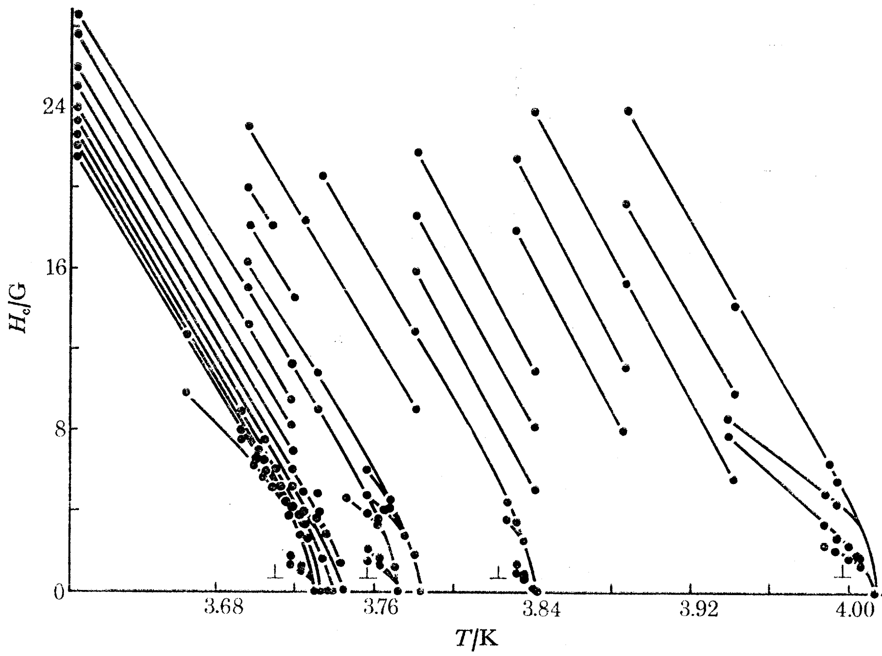

FIGURE 9. Graph of critical field $H_c(T, \epsilon)$ for whisker no. 23, of [100] axial orientation. The curve on the extreme left is for zero strain, and successive strain increments are 0.1 % To emphasize the nonlinear shift of the curves with strain, large portions of the first order transition surface have been included in the diagram. The change from second to first order transitions occurs at about 4×10^{-4} T (4 G) and is indicated by the onset of supercooling, which is drawn as a branch on the curve. Some points in transverse field are also shown and indicated $\perp$. (1 G = 10^{-4} T.)

Figure 9 shows $H_c(T, \epsilon)$ for whisker no. 23, which differed from the previous two whiskers in two respects: (i) it was of [100] axial orientation, so that T_c and the entire (H_c, T) curve shift non-linearly with strain (ii) it was a thicker whisker (as determined from its electrical resistance and by sectioning and examining it in an electron microscope after the experiment) so that $T'(\epsilon)$ lay closer to $T_c(\epsilon)$ than it would have done for a thinner whisker; the fields H' were only about 4 G†

† 1 G = 10^{-4} T.

as against about 12 G for the other whiskers. Thus not many points could be obtained for this whisker. (To emphasize the nonlinear shift of the curves with strain, large portions of the first order transition surface have been included in the diagram.) As usual, points in transverse field lie below the corresponding points in parallel field. Figure 10 shows some of the results obtained for the two-segment whisker no. 24. The dashed curve at the extreme left is that for zero strain, and (H_c, T) curves are shown at four other strain settings, corresponding to increments of 0.45 % in the strain of the sample as a whole; the strain of each segment can be calculated from the sizes of the two voltage signals across the whisker. This whisker was of [100] orientation and also happened to be fairly thick, so each segment gave rise to a family of curves very similar to those shown in figure 9 for whisker no. 23.

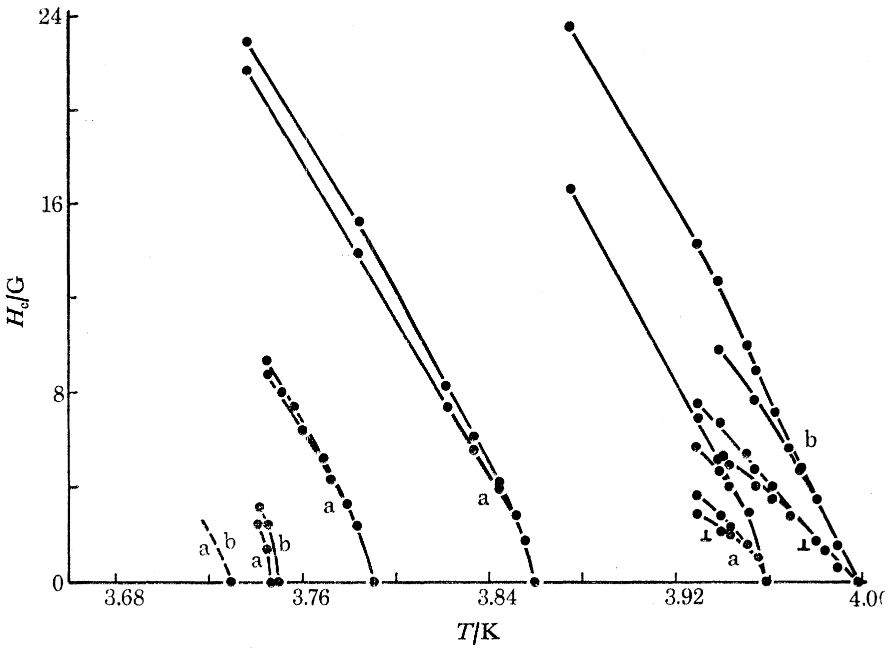

FIGURE 10. Values of $H_c(T, \epsilon)$ for the two-segment [100] whisker no. 24, plotted as a function of temperature T at total-strain increments of 0.045 %. For clarity, the curves of segments b are not shown for all strain values. (1 G = 10^{-4} T.)

The results of least squares fits to plots of H_c^2 against T are shown in table 3, and the slopes of such graphs are plotted as a function of strain for whiskers nos. 21 and P3, both of [001] orientation, in figures 11 *a*, *b*.

The largest source of error in these measurements is probably the inherent width of the transition, so that one must define $H_c(\epsilon, T)$ as the field at which the resistance of the sample has half its maximum value. The width possibly arises from the irregular cross section of the whisker; all the whiskers studied had a transition with a finite width, the thinner ones usually having a sharper transition than the thicker ones, and the width usually increasing with strain.

It was necessary to know the change of H_{00} with strain. This was estimated from measurements of $H_c(\epsilon, T)$ in the first order region, which were extrapolated to zero temperature and corrected for size effects (Rothberg 1972). In the first order region, H_T was distinguished from superheating and supercooling fields by the method described by Rothberg *et al.* (1971). Rothberg (1972) found that, for a whisker of a given orientation, H_{00} and T_c varied together with strain, e.g. parabolically for [100] and linearly for [001] whiskers. The results for eight whiskers, of three different orientations, could be summarized in the statement that

$$\mathrm{d}\ln H_{00}/\mathrm{d}\ln T_c = 1.2 \pm 0.1, \tag{6.3}$$

so that

$$\mathrm{d}\ln H_{00}/\mathrm{d}\epsilon_i = 13.4 \pm 1.4. \tag{6.4}$$

The large error on this value arises from errors in the extrapolation procedure. Values of H_{00} in table 3 were obtained from these data.

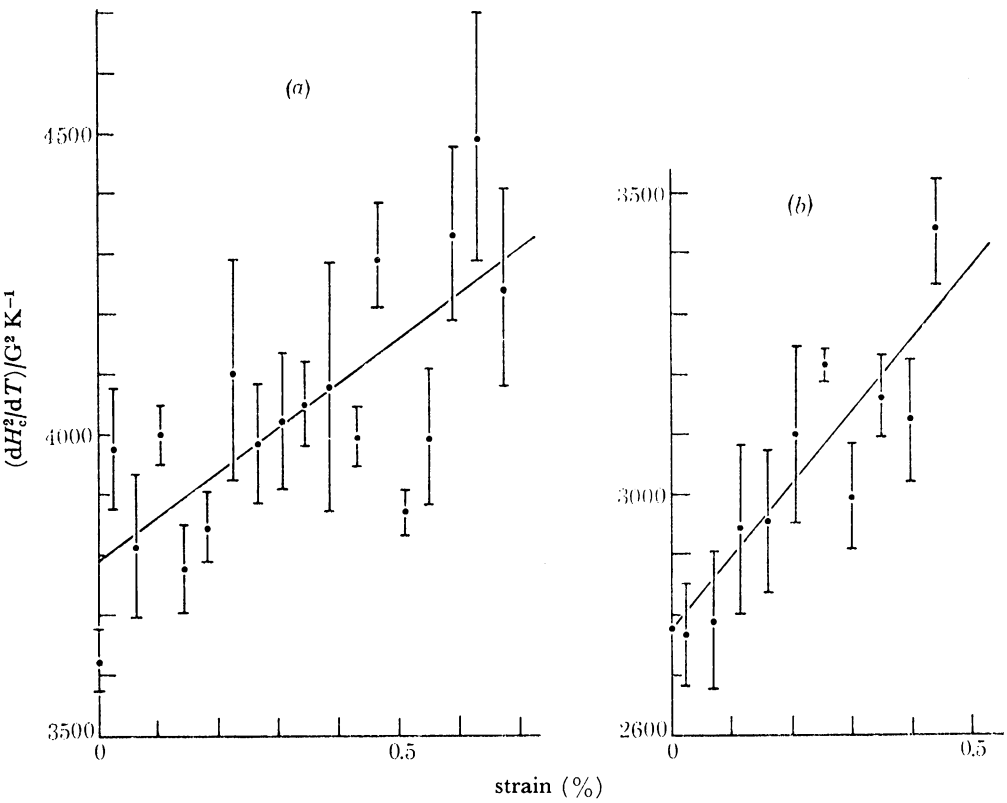

FIGURE 11. Variation with strain ϵ of the slopes $(\mathrm{d}H_c^2/\mathrm{d}T)$ of the points in the second order region shown in (*a*) figure 7*b* for the [001] whisker no. 21 and (*b*) figure 8*b* for the [001] whisker no. P3.

7. Application of theory to results at zero strain

Table 3 shows values of λ_{00}/r for four whiskers, calculated from the given slopes of graphs of H_c^2 against T, in accordance with (3.8). These values are given at various strains, but we will at present discuss only the zero-strain curves. The last column sets limits on the value of λ_{00}/r, using (3.9) and (3.6), so that

$$\lambda_{00}/r = 2(T_c - T')^{\frac{1}{2}}/(3T_c)^{\frac{1}{2}}. \tag{7.1}$$

We base our initial analysis on the assumption that the observed branch point is a true Landau critical point and not a singular point with $C = 0$ or a hypo-critical point, although the experimental results provide some evidence against this assumption. It is impossible to measure T'

TABLE 3. VARIATION WITH STRAIN OF THE SECOND ORDER TRANSITION CURVES AND RATIO λ_{00}/r FOR FOUR WHISKERS

strain (%)	slope $-\mathrm{d}H_c^2/\mathrm{d}T$ / $\mathrm{G^2\,K^{-1}}$‡	standard error in slope	$T_c(\epsilon)$ / K	$H_{00}(\epsilon)$/G (estimated from first order extrapolation)	λ_{00}/r (from slope and estimated $H_{00}(\epsilon)$)	λ_{00}/r (from estimates of the branching temperature T')
			(*a*) *whisker no.* 21 [001]			
0	3614	55	3.7249	315	0.092	0.077–0.091
0.024	3964	97	3.7396	312	0.098	0.10–0.109
0.065	3806	127	3.7577	—	—	0.102–0.109
0.11	3984	54	3.7693	324	0.094	0.095–0.109
0.15	3764	76	3.7840	—	—	0.10–0.112
0.19	3832	64	3.8019	328	0.092	0.10–0.115
0.23	4093	181	3.8161	—	—	0.10–0.11
0.27	3973	102	3.837	330	0.094	0.097–0.11
0.31	4017	117	3.8517	—	—	0.104–0.115
0.35	4046	76	3.8687	332	0.094	0.104–0.115
0.39	4073	208	3.8860	—	—	0.109–0.115
0.43	3984	50	3.9046	344	0.090	0.102–0.115
0.47	4288	84	3.9214	—	—	0.10–0.109
0.51	3875	42	3.9442	337	0.092	0.115–0.13
0.55	3988	112	3.9636	—	—	0.10–0.12
0.59	4324	146	3.9806	342	0.096	0.109–0.115
0.63	4484	203	3.999	—	—	0.10–0.11
0.67	4234	164	4.109	343	0.094	0.11–0.12
			transverse field			
0	594	26	3.7239	315	0.054†	0.077–0.091
0.67	720	56	4.0186	343	0.055†	0.11–0.12
			(*b*) *whisker no.* P3 [001]			
0	2829	133	3.7298	309	0.082	0.084–0.10
0.027	2769	78	3.7464	311	0.082	0.10–0.11
0.074	2791	112	3.7545	314	0.082	0.84–0.10
0.12	2942	146	3.7723	317	0.084	0.10–0.11
0.17	2956	116	3.7909	317	0.084	0.09–0.105
0.21	3101	150	3.8145	314	0.086	0.11–0.12
0.26	3210	33	3.8271	321	0.086	0.12–0.13
0.30	2998	82	3.8429	323	0.084	0.11–0.12
0.35	3162	64	3.8681	325	0.086	0.12–0.13
0.39	3125	95	3.8851	325	0.084	0.12–0.13
0.44	3438	84	3.9150	322	0.090	0.11–0.125
			(*c*) *whisker no.* 23 [100]			
0.08	1037	207	3.7299	303	0.052	—
0.16	1207	97	3.7316	—	—	—
0.24	1069	147	3.7353	—	—	—
0.32	1121	31	3.7411	—	—	—
0.41	966	57	3.7443	—	—	0.052–0.07
0.81	1067	77	3.7854	305	0.052	—
			(*d*) *whisker no.* 24 [100]			
0.53	1117	156	3.746	310	0.026	—
0.56	1259	146	3.7485	315	0.027	—
0.98	996	148	3.789	318	0.024	—
1.43	1289	140	3.858	322	0.027	—
1.87	941	21	3.9595	328	0.023	—
1.98	648	212	3.998	332	0.019	—

† Values in transverse field calculated assuming that the slope should be half as much as in parallel field (see (3.8)).

‡ 1 G = 10^{-4} T.

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experimentally but it is possible to set limits on T' by using temperatures bracketing the Landau critical point, at which the transition is of second and first order respectively. We then obtain a second estimate of λ_{00}/r by using (3.6) and (3.9). The values of λ_{00}/r obtained by the two methods agree satisfactorily, and are of the correct order of magnitude: if we assume that λ_{00} has a value of about 50 nm (Laurmann & Shoenberg 1949) then the results of table 3 predict that the radii of the [001] whiskers were about 0.55 μm while the radii of the [100] whiskers were about twice this value. These values of r are compatible with the estimates made electron-microscopically (by sectioning) or from the normal resistance of the whiskers at room temperature (where boundary scattering is negligible compared to phonon scattering) for which typical values were: 89 Ω for whisker no. P3 with a gauge length of 0.83 mm; and 20 Ω for the thicker whisker no. 23 with a gauge length of 0.88 mm. This gives average radii of (0.55 ± 0.04) μm and (1.2 ± 0.08) μm respectively, using the resistivity values of Burckbuchler & Reynolds (1968).

Several transition curves were studied well into the first order region, the most detailed of these being the zero-strain curve of whisker no. 21, in which measurements made on two different days agreed very well with each other. Measurements were also made for the same whisker at maximum strain (see figure 7*a*) and for whisker no. P3 at a strain of 0.35 % (see figure 8*a*). On these 'forked' curves, the lower branch of the curve represents observed supercooling fields, while the upper branch shows thermodynamic equilibrium fields. No superheating was observed in these cases.

Since the same equation (4.5) describes both the supercooling field and the thermodynamic equilibrium field in the second order region, a graph of $H^2_{\mathrm{s.c.}}$ against T should be a straight line for the supercooling points, continuous with the relevant points of the second order region. The supercooling points are plotted in figure 7*b* and figure 8*b* and it is seen that they do indeed lie on the same line; the supercooling is well described by theory. Since all the supercooling points measured in this series of experiments lie on the theoretical line, the supercooling of the whiskers under these conditions must be the maximum possible, so that the measured theoretical transition field is the limiting supercooling field, corresponding to curve 2 in figure 1*c*. It would also be possible for less supercooling to occur, corresponding to a curve such as 3 in figure 1*c*.

From (4.6), the points of the thermodynamic equilibrium curve in the first order region should lie on a straight line when plotted in the form of J against h^2_T, where the experimental quantity J is defined by

$$J = (h_T - 1)^2/(h^2_T - \delta t). \tag{7.2}$$

According to the theory,

$$J = \frac{16}{3}\frac{a_2}{b_2}\left(\frac{c_1}{b_1} + \frac{c_2}{b_2}h^2_T\right). \tag{7.3}$$

The graph should have a slope of $16a_2c_2/3b^2_2$, which (from (2.8) and (2.12)) is equal to 4.125. The intercept on the abscissa determines c_1.

Before plotting this graph, it was necessary to estimate T' and H' as accurately as possible for (*a*) whisker no. 21 at zero strain, (*b*) whisker no. 21 at maximum strain, and (*c*) whisker no. P3 at a strain of 0.35 %, so that points could be plotted in reduced form. The difference $H_T - H_{\mathrm{s.c.}}$ at a given temperature was plotted as a function of temperature as shown in figures 12*a*–*c* and a straight line could be drawn through these points, cutting the axis at a finite angle, so that the curves for the thermodynamic equilibrium field and for the supercooling field do not appear to be tangential to each other at the critical point, as the theory of the Landau critical point requires. The upper and lower limits on T' and H' established from these plots were used in plotting the

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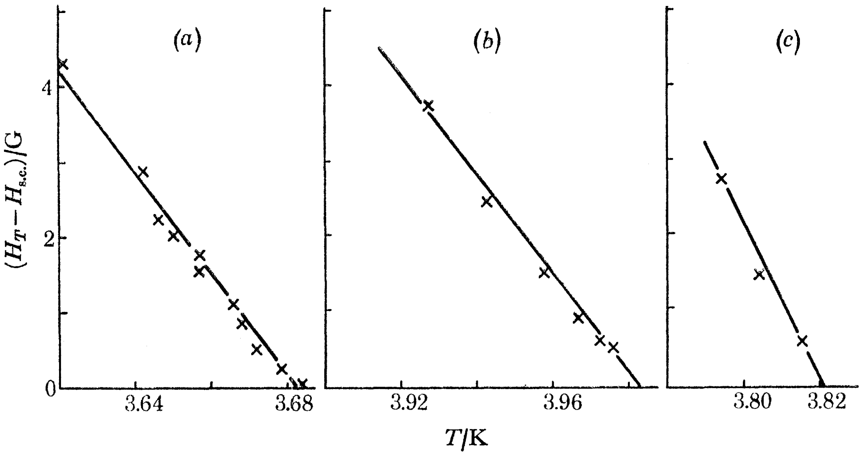

FIGURE 12. Branching of the thermodynamic critical field H_T from the supercooling field $H_{s.c.}$ as a function of temperature for (*a*) whisker no. 21 at zero strain, (*b*) whisker no. 21 at maximum strain, (*c*) whisker no. P3 at a strain of 0.35 %.

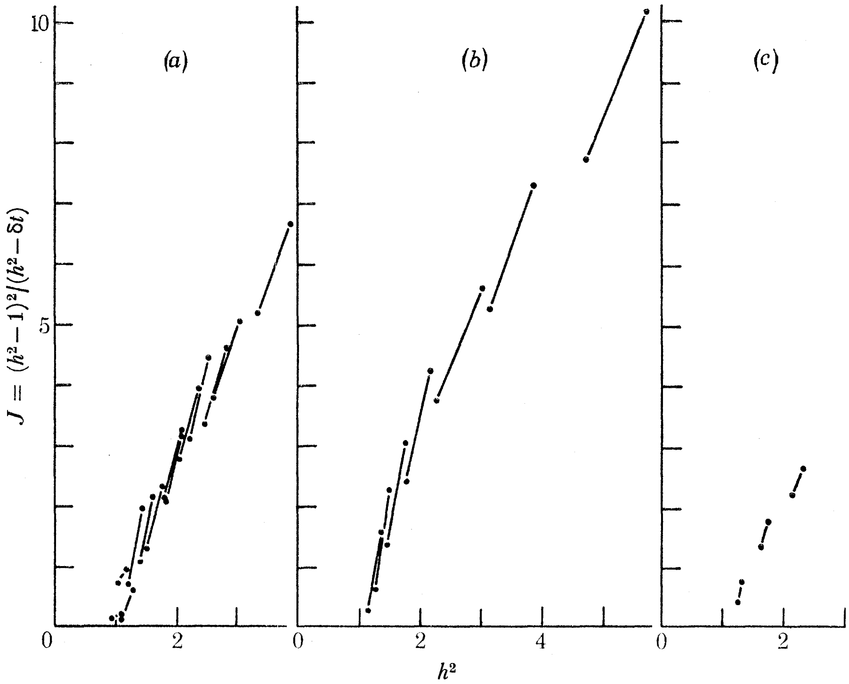

FIGURE 13. Variations with reduced field h^2 of the quantity $J = (h^2-1)^2/(h^2-\delta t)$ for (*a*) whisker no. 21 at zero strain, (*b*) whisker no. 21 at maximum strain, (*c*) whisker no. P3 at a strain of 0.35 %. Error bars were estimated by considering the accuracy with which (H', T') could be determined from graphs in figure 12. The slope of such graphs near $h^2 = 1$ should be 4.125, while the intercept on the abscissa gives the value of C at the Landau critical point. If the intercept is at $h^2 = 1$, then $C = 0$ at the critical point.

graphs of J against h^2 shown in figures 13*a–c* respectively; because of the uncertainty in T' and H' each experimental point has been plotted as an 'error bar'. The theory has been developed on the assumption that h^2 does not greatly exceed unity. We therefore plot figures 13*a–c* as required by (7.2), and draw tangents to the resulting curves at the point $h^2 = 1$. A line of slope 4.125 can be drawn tangential to the first few points of (*a*) and (*b*). When points in the range $1 \leqslant \delta t \leqslant 2$ are considered, the slopes are respectively 2.8 ± 0.2, 3.4 ± 0.2 and 2.2 ± 0.2.

The intercept on the abscissa appears to be at 1 ± 0.1, indicating that $C \simeq 0$ at the critical point. If indeed $C \simeq 0$ at the Landau critical point, (4.12) to (4.14) predict that, as is observed, the curves of h^2 versus δt for the thermodynamic equilibrium and the supercooling transition should not be tangential at the Landau critical point, but should have slopes of 1.32 and 1 respectively. The observed ratios of these slopes, 1.28 for the most reliable set of results (whisker no. 21 at zero strain) and 1.31 and 1.63 for the less reliable sets (no. 21 at maximum strain and no. P3 at 0.35 % strain respectively), with probable errors of ± 0.1, ± 0.1 and ± 0.2, are compatible with this prediction.

The value of C at the Landau critical point depends on the size of the whisker, and we are led to the conclusion that whisker no. 21, for which we have two sets of measurements at different strains, was fortuitously of such a size as to give $C \simeq 0$ at the Landau critical point, while whisker no. P3 is almost the same size, and the observations are too sparse to allow a detailed analysis.

It is perhaps remarkable that our experimental results should conform closely to those predicted if $C = 0$ at the Landau critical point, and we may ask if there are any circumstances in which this result would be true for whiskers of arbitrary size. This would require a strong dependence of c_1 on temperature, contrary to the spirit of a Landau expansion. In fact, if A, B and C in (2.11) vanish simultaneously for whiskers of all radii r, with a_2, b_2 and c_2 independent of r, a_1 given by (2.2) and a_2, b_2 and c_2 by (2.12) and (2.8), we must have, in addition to the results $H' \propto 1/r$, $T_c - T' \propto 1/r^2$, the quite unphysical dependence $c_1 \propto 1/(T_c - T')$.

II. SAMPLES UNDER ELASTIC STRAIN

8. The thermodynamic order of the transition in a stressed superconductor

It is not immediately obvious that the phase transition in a stressed superconductor in the absence of a magnetic field will be of second order. Just as the normal–superconducting transition leads to a finite change in the magnetic induction in a sample exposed to a constant magnetic field, so it leads to a finite change in the elastic strain in a sample exposed to a constant stress. The transition in the former case is of first order: should it not be of first order also in the second case? Indeed, we might argue that the transition produces a finite change in the elastic constants, and so leads to a finite change in the volume of a sample under hydrostatic pressure. Such an argument is erroneous. The standard result for the difference between the volume $v^s(H_c)$ of the superconducting sample in the critical field H_c, and the volume of the normal sample v^n, is (e.g. (3.17) of Shoenberg 1965)

$$v^n - v^s(H_c) = H_c v^s(H_c)\,(\partial H_c/\partial P)_T/4\pi, \tag{8.1}$$

and this certainly vanishes for any transition in the absence of a magnetic field, where $H_c = 0$. The derivation of (8.1) proceeds by a consideration of the Gibbs free energies of the normal and the superconducting states. These Gibbs free energies are expressed in terms of P, T and H as independent variables, and it is not assumed that $P = 0$; nor it is assumed that the transition is of second order.

We may illustrate this somewhat surprising result by considering a sample brought from the state A in figure 14, where it is normal at zero pressure at a temperature just above $T_c(0)$, either to the normal state C or to the adjacent superconducting state F, both under pressure ΔP at a temperature $T_c(\Delta P)$. If K^n and K^s represent the compressibilities in the normal and the superconducting states, and α^n and α^s the corresponding coefficients of thermal expansion, we have

$$v_B - v_A = -vK^n\Delta P, \tag{8.2}$$

$$v_C - v_B = v\alpha^n(\partial T_c/\partial P)_H \,\Delta P, \tag{8.3}$$

$$v_A - v_D = 0, \tag{8.4}$$

$$v_D - v_E = -v\alpha^s(\partial T_c/\partial P)_H \,\Delta P \tag{8.5}$$

and

$$v_E - v_F = vK^s\Delta P. \tag{8.6}$$

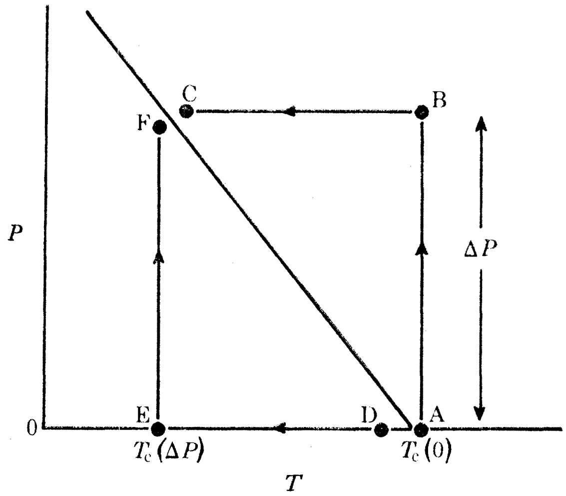

FIGURE 14. Paths by which a superconductor is brought from the normal state just above $T_c(0)$ to a state at pressure ΔP and temperature $T_c(\Delta P)$.

Adding these five equations, we find

$$v_C - v_F = v\Delta P[(K^s - K^n) - (\alpha^s - \alpha^n)\,(\partial T_c/\partial P)_H]. \tag{8.7}$$

We now substitute the values of $K^s - K^n$ obtained from (3.20) and (3.21) of Shoenberg (1965) by putting $H_c = 0$, namely

$$K^s - K^n = (\partial H_c/\partial P)_T^2/4\pi \tag{8.8}$$

and

$$\alpha^s - \alpha^n = -(\partial H_c/\partial T)_P\,(\partial H_c/\partial P)_T/4\pi, \tag{8.9}$$

obtaining

$$v_c - v_F = v\frac{\Delta P}{4\pi}\left(\frac{\partial H_c}{\partial P}\right)_T \left[\left(\frac{\partial H_c}{\partial P}\right)_T + \left(\frac{\partial H_c}{\partial T}\right)_P \left(\frac{\partial T_c}{\partial P}\right)_H\right] = 0. \tag{8.10}$$

The change of volume associated with the different compressibilities in the normal and superconducting states is exactly compensated (to first order in ΔP) by the change of volume associated with the different thermal expansion coefficients of the two states. Clearly, a finite stress may induce a change in the order of the transition (and we can find situations in the neighbourhood of the Landau critical point of a small sample where it will do so). What we have shown is that a small stress will not *in general* cause the order of the phase change to alter.

9. Analysis of phase diagrams of strained whiskers using only Ginsburg–Landau-type theory

Although it was in fact an axial strain component ϵ_i which was measured experimentally, it is preferable to discuss the system in terms of stress components σ_i, since a single stress component can be applied to the sample, while it is not possible to impose a single component of strain. In this experimental section strain ϵ is often used to indicate the axial strain component actually imposed, but in the discussion that follows we use σ.

Using the Ginzburg–Landau type theory developed in part I of this paper, we can draw conclusions about the second order transition surface in (H, T, ϵ) space, and can also estimate the change with strain of λ_{00}/r.

As shown in table 3, the graphs of H_c^2 against T were straight lines (to 2 % accuracy) for strains up to 0.7% of whiskers nos 21 and P3, which were of [001] orientation, and also (to lesser accuracy) for strains up to 2 % of whiskers nos 23 and 24, which were of [100] orientation. The entire transition surface in (H, T, ϵ) space is therefore well described at any given strain by the Ginzburg–Landau theory developed above; if the transition surface is indeed of second order, we are justified in later applying the Ehrenfest equations to it. For the present, we can regard strain as a mechanism by which one superconductor is continuously converted to a different superconductor, characterized by a different H_{00}, T_c and λ_{00}/r. We can then use our results to see how λ_{00}/r varies with strain. (For simplicity we regard λ_{00}/r as a single parameter, since $\partial \ln r/\partial\epsilon_i$ is known, and is small.)

From figures 11*a*, *b* and from table 3 we obtain values of

$$d[\ln (\partial H_c^2/\partial T)_{\epsilon 3}]/d\epsilon_3 = 20 \pm 4, \tag{9.1}$$

for whisker no. 21 and

$$d[\ln (\partial H_c^2/\partial T)\epsilon_3]/d\epsilon_3 = 43 \pm 7, \tag{9.2}$$

for whisker no. P3, where both whiskers are of the same orientation, namely [001].

From (3.8),

$$d \ln (\partial H_c^2/\partial T) = 2d \ln H_{00} + 2d \ln (\lambda_{00}/r) - d \ln T_c, \tag{9.3}$$

where the derivatives can be taken with respect to either σ_i or ϵ_i. Using the latter, and using (6.4) and (6.1), we obtain

$$2d \ln (\lambda_{00}/r)/d\epsilon_3 = 5 \pm 15 \tag{9.4}$$

for whisker no. 21, and

$$2d \ln (\lambda_{00}/r)/d\epsilon_3 = 27 \pm 13 \tag{9.5}$$

for whisker no. P3.

The disagreement between the two whiskers in this respect is also shown by the behaviour of T' as a function of strain (see figures 7 (*a*) and 8 (*a*)). Because of (6.1), an increase in λ_{00}/r with strain will give rise to an increase in $T_c - T'$. Whisker no. P3 shows an increase with strain in both these quantities, while for whisker no. 21 they both remain roughly constant. The increase of λ_{00}/r with strain in the case of whisker no. P3 is comparable with the changes in T_c and H_{00}.

We do not understand the difference in the behaviour of these two whiskers. If we combine the two sets of observations we obtain

$$d[\ln (\partial H_c^2/\partial T)]/d\epsilon_3 = 32 \pm 11, \tag{9.6}$$

and

$$2d \ln (\lambda_{00}/r)/d\epsilon_3 = 16 \pm 14. \tag{9.7}$$

The second order regions of the thicker whiskers were not extensive enough for $d \ln (\lambda_{00}/r)/d\epsilon_1$ to be estimated with any accuracy for whiskers of [100] orientation. As seen in table 3, whisker no. 24 was strained to $\epsilon \simeq 2$ % and λ_{00}/r then changed considerably.

The values of $\partial H_c^2/\partial T$ obtained in transverse field are about one sixth those in parallel field, while they should be half as big on the Ginzburg model, as discussed in §§2 and 3 above. It is possible that this discrepancy is caused by the irregular cross section of the whisker, as discussed in §6 above. We do not have sufficient data in transverse field to be able to say whether this ratio of 1/6 is typical of whiskers or varies from sample to sample, as it ought to if the irregular cross section of the whisker is an important factor.

10. The Ehrenfest relations for a small elastically strained superconductor

Changes in the Gibbs free energy of the sample can be written (Seraphim & Marcus 1962) in terms of the magnetization M, the volume v and the entropy S, giving

$$\mathrm{d}G = -S\,\mathrm{d}T - M\,\mathrm{d}H - v\sum_{i=1}^{6}\epsilon_i\,\mathrm{d}\sigma_i. \tag{10.1}$$

The quantities S, M and $v\epsilon_i$ are first derivatives of G, and must be continuous at a second order transition. At any point on the transition surface we have the condition $M^{\mathrm{n}} = M^{\mathrm{s}}$, while $M^{\mathrm{n}} + \mathrm{d}M^{\mathrm{n}} = M^{\mathrm{s}} + \mathrm{d}M^{\mathrm{s}}$ at an adjacent point, so that $\mathrm{d}M^{\mathrm{n}} = \mathrm{d}M^{\mathrm{s}}$ on the second order surface. The increment in magnetization is given by

$$\mathrm{d}M^{\mathrm{n}} = (\partial M^{\mathrm{n}}/\partial H)_{T,\sigma i}\,\mathrm{d}H + (\partial M^{\mathrm{n}}/\partial T)_{H,\sigma i}\,\mathrm{d}T + (\partial M^{\mathrm{n}}/\partial\sigma_i)_{H,T}\,\mathrm{d}\sigma_i$$

and similarly for $\mathrm{d}M^{\mathrm{s}}$, so that the changes in the differentials are given by

$$\Delta^{\mathrm{ns}}(\partial M/\partial H)_{T,\sigma i}\,\mathrm{d}H + \Delta^{\mathrm{ns}}(\partial M/\partial T)_{H,\sigma i}\,\mathrm{d}T + \Delta^{\mathrm{ns}}(\partial M/\partial\sigma_i)_{H,T}\,\mathrm{d}\sigma_i = 0. \tag{10.2}$$

Similar relations exist for the entropy S and for $v\epsilon_i$.

We now put the differentials $\mathrm{d}\sigma_i$, $\mathrm{d}H$ and $\mathrm{d}T$ in (11.2) successively equal to zero, and introduce symbols for the uniaxial coefficient of thermal expansion $\alpha_i = \partial\epsilon_i/\partial T$, for the diagonal components of the elastic moduli $s_{ii} = \partial\epsilon_i/\partial\sigma_i$ and for the thermal capacity at constant σ_i and H, $C_{\sigma H}$. The repeated indices do not here imply a summation. We also use the Maxwell-type relations

$$\left.\begin{aligned}(\partial M/\partial T)_{H,\sigma} &= -(\partial S/\partial H)_{T,\sigma},\\ (\partial(v\epsilon_i)/\partial H)_{T,\sigma} &= -(\partial M/\partial\sigma_i)_{H,T},\\ \text{and}\qquad (\partial S/\partial\sigma_i)_{H,T} &= -(\partial(v\epsilon_i)/\partial T)_{H,\sigma},\end{aligned}\right\} \tag{10.3}$$

and obtain the Ehrenfest equations

$$\mathrm{d}\sigma_i = 0:\quad (\partial H/\partial T)_\sigma = -\Delta^{\mathrm{ns}}(\partial M/\partial T)_{H,\sigma}/\Delta^{\mathrm{ns}}(\partial M/\partial H)_{T,\sigma}, \tag{10.4}$$

$$\mathrm{d}H = 0:\quad (\partial T/\partial\sigma_i)_H = -\Delta^{\mathrm{ns}}(\partial M/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}}(\partial M/\partial T)_{H,\sigma} \tag{10.5}$$

and

$$\mathrm{d}T = 0:\quad (\partial H/\partial\sigma_i)_T = -\Delta^{\mathrm{ns}}(\partial M/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}}(\partial M/\partial H)_{T,\sigma}. \tag{10.6}$$

Similarly, using the relations analogous to (10.2) which hold for the other first derivatives S and $v\epsilon_j$, we obtain

$$\begin{aligned}\mathrm{d}\sigma_i = 0:\quad (\partial H/\partial T)_\sigma &= -\Delta^{\mathrm{ns}}(\partial S/\partial T)_{\sigma,H}/\Delta^{\mathrm{ns}}(\partial S/\partial H)_{T,\sigma}\\ &= +\Delta^{\mathrm{ns}}(T^{-1}C_{\sigma H})/\Delta^{\mathrm{ns}}(\partial M/\partial T)_{\sigma,H},\end{aligned} \tag{10.7}$$

$$\begin{aligned}\mathrm{d}H = 0:\quad (\partial T/\partial\sigma_i)_H &= -\Delta^{\mathrm{ns}}(\partial S/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}}(\partial S/\partial T)_{H,\sigma}\\ &= +\Delta^{\mathrm{ns}}v\alpha_i/\Delta^{\mathrm{ns}}(T^{-1}C_{\sigma H}),\end{aligned} \tag{10.8}$$

$$\mathrm{d}T = 0\colon\quad (\partial H/\partial\sigma_i)_T = -\Delta^{\mathrm{ns}}(\partial S/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}}(\partial S/\partial H)_{T,\sigma}$$
$$= -\Delta^{\mathrm{ns}} v\alpha_i/\Delta^{\mathrm{ns}}(\partial M/\partial T)_{\sigma,H}, \tag{10.9}$$
$$\mathrm{d}\sigma_i = 0\colon\quad (\partial H/\partial T)_\sigma = -\Delta^{\mathrm{ns}} v(\partial\epsilon_i/\partial T)_{H,\sigma}/\Delta^{\mathrm{ns}} v(\partial\epsilon_i/\partial H)_{T,\sigma}$$
$$= +\Delta^{\mathrm{ns}} v\alpha_i/\Delta^{\mathrm{ns}}(\partial M/\partial\sigma_i)_{H,T}, \tag{10.10}$$
$$\mathrm{d}H = 0\colon\quad (\partial T/\partial\sigma_i)_H = -\Delta^{\mathrm{ns}}(v\,\partial\epsilon_i/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}}(v\,\partial\epsilon_i/\partial T)_{H,\sigma}$$
$$= -\Delta^{\mathrm{ns}} v s_{ii}/\Delta^{\mathrm{ns}} v\alpha_i \tag{10.11}$$

and

$$\mathrm{d}T = 0\colon\quad (\partial H/\partial\sigma_i)_T = -\Delta^{\mathrm{ns}}(v\,\partial\epsilon_i/\partial\sigma_i)_{H,T}/\Delta^{\mathrm{ns}} v(\partial\epsilon_i/\partial H)_{T,\sigma}$$
$$= +\Delta^{\mathrm{ns}} v s_{ii}/\Delta^{\mathrm{ns}}(\partial M/\partial\sigma_i)_{H,T}. \tag{10.12}$$

Only six of these nine equations are independent, since

$$(\partial H/\partial T)_\sigma\,(\partial T/\partial\sigma_i)_H\,(\partial\sigma_i/\partial H)_T = -1. \tag{10.13}$$

The equations (10.7), (10.9), (10.10) and (10.12) have been written in such a form that each involves both a derivative of M and one of the quantities $C_{\sigma H}$, α_i or s_{ii}. Equations (10.8) and (10.11) do not involve M and their right hand sides can be equated to give the identity

$$\Delta^{\mathrm{ns}}(v\alpha_i)/\Delta^{\mathrm{ns}}(T^{-1}C_{\sigma H}) = -\Delta^{\mathrm{ns}} s_{ii}/\Delta^{\mathrm{ns}}\alpha_i, \tag{10.14}$$

which has been derived by Pippard (1960) for the case of a superconductor under hydrostatic pressure and found to agree satisfactorily with the then available data for bulk tin. We now provide a similar verification for tin under uniaxial stress along the tetragonal axis, and we also verify the Ehrenfest relations (10.8) and (10.11) as well as applying (10.5) to our measurements.

11. Applications of the Ehrenfest relations to experimental data on strained whiskers

Measurements of the required changes at the transition of the quantities $C_{\sigma H}$, α_i and s_{ii} have been made only at zero strain, and only for large samples, the experimental procedure being to make the measurement as a function of temperature and to extrapolate to T_c. Because of the argument given in §5 above, it is valid to use these values when discussing the behaviour of our small samples.

The following values have been obtained:

(*a*) Corak & Satterthwaite (1956) and Cochran (1962) measured the specific heat as a function of temperature both in the superconducting state ($H = 0$) and in the normal state (in the presence of a field) and found that, for bulk tin, $\Delta^{\mathrm{ns}}(C(T_c)/T_c) = 2.7\,\mathrm{mJ\,mol^{-1}\,K^{-2}}$ so that, for a sample of volume v,

$$\Delta^{\mathrm{ns}}(C(T_c)/T_c) = 1.67\,v\times 10^{-4}\,\mathrm{J\,K^{-2}}. \tag{11.1}$$

(*b*) White (1964) measured the coefficient of thermal expansion as a function of temperature by a capacitative method, obtaining

$$\Delta^{\mathrm{ns}}\alpha_3 = 8.5\times 10^{-8}\,\mathrm{K^{-1}} \tag{11.2}$$

for the value along the [001] axis, while his value along the [100] axis is virtually zero.

(*c*) Gibbons & Renton (1959) measured the velocity of sound in the normal and superconducting states and extrapolated to T_c to obtain a change in the elastic modulus of

$$\Delta^{\mathrm{ns}} s_{33}/s_{33} = (32\pm 4)\times 10^{-7}.$$

Rayne & Chandrasekhar's (1960) value of $s_{33} = 11.5\times 10^{-13}\,\mathrm{cm^2/dyn}$ then gives

$$\Delta^{\mathrm{ns}} s_{33} = 3.5\times 10^{-18}. \tag{11.3}$$

These values can be substituted into equation (10.14), when the left-hand side is found to give $5.1\times10^{-11}\,\mathrm{K\,cm^2\,dyn^{-1}}$ and the right hand side $4.1\times10^{-11}\,\mathrm{K\,cm^2\,dyn^{-1}}$, which is in good agreement in view of the errors quoted by the individual authors.

Our measurements now allow a verification of the Ehrenfest relations (10.8) and (10.11). The values in (11.1), (11.2) and (11.3) inserted into (10.8) predict that $\partial T_c/\partial\sigma_3$ should be 5×10^{-11} K cm²/dyn, while (10.11) predicts that $\partial T_c/\partial\sigma_3$ should be 4.5×10^{-11} K cm²/dyn. The actual value of $\partial T_c/\partial\sigma_3$ at zero strain (see (6.2)) is $(4.83\pm0.12)\times10^{-11}$ K cm²/dyn, so that the Ehrenfest relations have been verified by our measurements in the case of zero strain and zero field.

Returning now to (5.12), (5.13), (5.14) and (5.15), we see that all these second derivatives of G vary with field and temperature in the same way in the second order region (i.e. they are all inversely proportional to the coefficient B), so that the Ehrenfest relations between them will be satisfied throughout this region.

Since all the other Ehrenfest relations explicitly involve the magnetization M, which we have not measured directly, we can relate them to our measurements only by the use of a theoretical formula, such as (5.4). For example, (5.14) may be written, when $t\simeq1$ and $H\simeq0$,

$$(\partial M/\partial\sigma_i)_{H,T}\simeq\frac{-vH}{8\pi}\left(\frac{r}{\lambda_{00}}\right)^2\frac{T}{T_c}\frac{\partial\ln T_c}{\partial\sigma_i}. \tag{11.4}$$

By using (5.12), this becomes

$$(\partial T/\partial\sigma_i)_H\simeq T/T_c(\partial T_c/\partial\sigma_i)_{H=0}. \tag{11.5}$$

This predicts that, while $t\simeq1$, the curves shift rigidly with strain, at a rate determined by $\mathrm{d}T_c/\mathrm{d}\sigma_i$. Figures 7*a*, 8*a*, 9 and 10 show that it is indeed a fair approximation to say that the (H_c, T) curves shift rigidly with strain near $T_c(\epsilon)$, namely linearly for a [001] whisker and parabolically for a [100] whisker.

12. Conclusion

Transition surfaces of 'moderately' small, elastically strained superconductors (tin whiskers) have been plotted (I) at fixed strain, (II) as a function of strain, in the range of temperature near that point at which the transition changes from one of second order to one of first order in the Ehrenfest sense. The point at which the order of the transition changes is described as a critical point of Landau type, and we have derived the form of the variation in the specific heat and other second derivatives of the Gibbs free energy near this point. Since the magnetization of the sample must be expressed as a sum of powers of the order parameter up to ψ^6, it was thought necessary to extend Ginzburg's (1958) analysis by including a term in ψ^6 in the free energy even in the field-free case. The corresponding coefficient was estimated from experimental data, and found to be negative. The observed thermodynamic transition curve branched at a finite angle from that describing supercooling; in general the theory predicts that these two curves should be tangential at the Landau critical point. A way of explaining these observations is suggested elsewhere (Nabarro & Bibby 1974).

We have also shown, both experimentally and theoretically, that the transition of a small superconductor near T_c remains of second order under homogeneous elastic stress.

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Appendix. Description of a 'small' superconductor

The free energy G given by (2.7) may alternatively be expressed in terms of the energy gap Δ in the form

$$G = a_1\Delta^2 + \tfrac{1}{2}b_1\Delta^4 + m_1H^2\lambda^{-2} - m_2H^2\lambda^{-4} + m_3H^2\lambda^{-6}, \tag{A 1}$$

where m_1, m_2 and m_3 are given by (2.8) and a_1 and b_1 are redefined. We now express λ^{-2} in terms of Δ by

$$\lambda^{-2} = l_1\Delta^2 - l_2\Delta^4 + l_3\Delta^6. \tag{A 2}$$

This gives rise to a more general expression than (2.6). Adding a term $\tfrac{1}{3}c_1\Delta^6$ as before to (A 1) and inserting (A 2) we obtain

$$G = -a_1\Delta^2 + \tfrac{1}{2}b_1\Delta^4 + \tfrac{1}{3}c_1\Delta^6 + m_1H^2l_1\Delta^2 + H^2(m_1l_2 + m_2l_1^2)\,\Delta^4 + H^2(m_1l_3 + 2m_2l_1l_2 + m_3l_1^3)\,\Delta^6, \tag{A 3}$$

which is of the same form as (2.10) and (2.11). The coefficients a_2, b_2 and c_2 are now given not by (2.12) but by

$$a_2 = m_1l_1, \quad b_2 = 2(m_1l_2 + m_2l_1^2) \quad \text{and} \quad c_2 = 3(m_1l_3 + 2m_2l_1l_2 + m_3l_1^3). \tag{A 4}$$

Since ψ and Δ are implicit variables which do not appear in the final formula, many of the results of §§1–5, for the Ginzburg limit, apply also in the general case. If the same temperature dependences are used for a_1 and b_1, then all the results can be taken over.

In the Ginzburg–Landau limit of a clean specimen with a radius r such that there exists a temperature T' such that $r = \sqrt{(3)}\,\lambda(T')$ with $T_c - T' \ll T'$ we take $l_2 = 0$, $l_3 = 0$ in (A 3) and (A 4). Bardeen (1962) discusses a specimen with $r < \lambda(0) < \xi_0$, where boundary scattering necessarily makes the sample 'dirty'. Bardeen's form of the free energy (his equation (5.2)) has $m_1 \neq 0$, $m_2 = 0$, $m_3 = 0$ (see his equation (A 7)); since his sample is so small, terms of higher order in r/λ are neglected. In equation (5.2) of Bardeen (1962), $l_1 \neq 0$, $l_2 \neq 0$, $l_3 = 0$ (see his equation (3.13), which is expanded to order Δ^4 in his (5.2); the term in c_1 need not be introduced in (A 3) in this case). The Ginzburg–Landau and Bardeen cases can thus be made formally equivalent, so that G has the same properties. As seen in (5.4) to (5.6) of Bardeen (1962), a temperature (denoted t_1), analogous to T' in the body of the paper, is predicted by Bardeen's theory, such that the transition is of second order above t_1 and of first order below it. Here, however, it is not the sample size but the material parameters $N(0)$ and V which determine the critical point.

We should like to thank Professor J. Bardeen (1973) for confirming our detection of an error in (5.2) *et seq.* of his paper (Bardeen 1962) and for pointing out another error in this equation. His term a_2 should be prefaced by a factor $\frac{1}{2}$, and the term $\beta^3\Delta^4$ should be prefaced by $\frac{1}{24}$ instead of $\frac{1}{12}$.

It is interesting to compare Bardeen's formula for the magnetic energy with that used in the Ginzburg–Landau limit in the body of the paper (equation (2.7)). Near T_c, where $\lambda(T) \gg r$ the two formulae are equivalent. We use the results of weak-coupling isotropic B.C.S. theory: $N(0)\,\Delta_0^2 = H_{c,b}^2(0)/4\pi$ and $\xi_0 = \hbar v_F/\pi\Delta_0$, and also use Bardeen's (1962) equations (A 7) and (3.13). Bardeen's formula (5.1) for the magnetic energy is $\frac{1}{2}aH^2N(0)\,\Delta_0\Delta\tanh(\frac{1}{2}\beta\Delta)$, which can be written as

$$\tfrac{1}{2}g_L\left(\frac{r}{\lambda}\right)^2\frac{H^2}{4\pi}\frac{\xi_0\lambda_L^2}{l\lambda^2}.$$

Since $g_L = \frac{1}{8}$ for a cylinder in parallel field (Bardeen 1962, table I), this equation is equivalent to the third term in (2.7) in our paper, provided that we write $\lambda^2 = \xi_0\lambda_L^2/l$, where l is the mean free path in the sample. It is well known (Lynton 1969) that such a procedure gives good agreement for small or impure specimens.

It is also of interest that Bardeen's (1962) equation (5.8) for the shape of the transition curve near T_c predicts that H_c^2 is proportional to $(T_c - T)$, in agreement with (3.4) in our work.