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# Theory of a superconductor with a tricritical point

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Abstract. The Ginzburg-Landau theory of a superconductor with a tricritical point on its phase transition line in the (T, P) plane is formulated. The tricritical point divides the transition line into two parts. One part is the line of first-order transitions, the other that of second-order transitions. The magnetic properties of such a superconductor are different from both type I and type II superconductors. In a part of the phase diagram, the transition into the mixed state is a first-order transition. The Meissner phase can always coexist with the normal phase. The assumption of the existence of a tricritical point makes it possible to interpret the superconducting phase diagram of UPt<sub>3</sub> in terms of a one-component order parameter.

### **1. Introduction**

There is still no satisfactory theoretical description of the properties of heavyfermion superconductors. In contrast to usual superconductors, which obey the weakcoupling BCS theory, they have two types of anomaly: (i) the power-law temperature dependencies of their thermodynamic and kinetic properties; and (ii) the observation of more than one phase transition line within the superconducting regime for these compounds. The second anomaly manifests itself in a clear way in UPt<sub>3</sub>, where two additional transition lines are observed, which is considered as an indication of the existence of three different phases (for a review see [1]). Both kinds of anomaly can naturally be explained by the BCs theory; if the pairing in these materials is assumed to be unconventional, i.e. at the superconducting transition, except for the gauge symmetry, some other symmetries of the normal phase are broken. Lowering of symmetry can impose the existence of zeros in a superconducting gap, which would explain the observed power laws. A multi-component order parameter can be associated with unconventional pairing, which opens up the possibility for the existence of different superconducting phases. The superfluid phases of <sup>3</sup>He exemplify both features very well. The assumption that the pairing in heavy fermions is of an unconventional nature is the realm of main stream research in theoretical efforts, in order to interpret the properties of these superconductors. In particular, several interpretation schemes of the complex phase diagram of UPt<sub>3</sub> have been suggested. Different representations of the symmetry group of UPt<sub>3</sub> were probed for its order parameter (for a review see [2]). Unfortunately, none of the suggested schemes gave, until now, a satisfactory description of the observed phase diagram.

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It has, as of yet, not been properly appreciated that an understanding of the properties of the superfluid phases of <sup>3</sup>He, except for unconventional pairing, requires another important development in the BCs theory. This is the introduction of strongcoupling corrections, i.e. terms in energy, which are of next to the leading order in a ratio of superconducting gap to characteristic energy of a normal state which, in the case of <sup>3</sup>He, is the Fermi energy [3]. Without introducing these corrections, the A phase would not exist as being thermodynamically stable. It has already been pointed out [4] that strong-coupling effects can be even more pronounced in such anomalous materials as heavy-fermion superconductors. Under such circumstances the weak-coupling BCS theory would no longer apply, and one could only rely on a phenomenological theory. Strong-coupling effects do not change the structure of the Ginzburg-Landau theory. The difference caused by the introduction of strong coupling is that the coefficients entering this theory cannot be calculated from the BCS theory, and have to be considered, as they initially were, as phenomenological parameters. In particular, the fourth-order term in the expansion of the free energy in powers of the order parameter need not be definitely positive. Removal of this restriction makes it possible for a superconducting transition to be of first order. Some other changes in the thermodynamic properties appear as well. All these changes make it possible to formulate an alternative interpretation of the phase diagram of UPt<sub>3</sub>, which does not exploit a multi-component order parameter [5].

In the following three sections we consider the thermodynamic properties and the temperature dependence of the critical magnetic field of a superconductor for which the fourth-order term in the Landau expansion of the free energy can take both positive and negative values, depending on pressure or temperature. Application of the developed scheme to  $UPt_3$  is discussed in section 5.

The theory does not depend on a particular mechanism, which allows the fourthorder terms to be negative. Another parameter, which is assumed to be small in the standard BCS theory, is the ratio of interatomic distance to the electron mean free path. When this parameter is not small one can also expect substantial deviations from the predictions of the BCS theory. In particular, Marikhin [6] has shown recently, in connection with the phase diagram of  $U_{1-x}$ Th<sub>x</sub>Be<sub>13</sub>, that for a multi-component order parameter the anisotropic scattering on impurities at sufficiently large doping can change the character of the phase transition into a superconducting state from second to first order. The incorporation of a multi-component order parameter in the developed scheme, although straightforward, is technically rather complicated. It is better to defer this discussion until such necessity arises. It is unlikely that the mechanism considered by Marikhin is operative in UPt<sub>3</sub>, since many data for this material were obtained with clean samples, where the mean free path of the carriers is much greater than the coherence length [7].

## 2. Thermodynamics of a superconductor with a TCP

We start from the Landau expansion of the thermodynamic potential of a superconductor in powers of the order parameter, which is assumed to be a one-component complex function  $\psi$ 

$$\phi_{\rm s}(P,T,|\psi|^2) = \phi_{\rm n}(P,T) + a(P,T)|\psi|^2 + \frac{1}{2}b(P,T)|\psi|^4 + \frac{1}{3}d(P,T)|\psi|^6.$$
(1)

A second-order phase transition line is defined by the conditions  $a(P,T) = \alpha(T - T_c) = 0$ , b(P,T) > 0. It can happen [8] that, at a certain point  $(T_t, P_t)$ 

on this line, the coefficient b(P, T) turns to zero and changes its sign. This is a so-called critical point of the second-order transition, or a tricritical point (TCP). In a region b(P,T) < 0 a phase transition is of first order and takes place on a line defined by the following conditions:

$$\partial \phi_{\rm s}(P,T,|\psi|^2)/\partial |\psi|^2 = 0 \tag{2}$$

$$\phi_{\mathbf{s}}(P,T,|\psi|^2) = \phi_{\mathbf{n}}(P,T). \tag{3}$$

From condition (2), and with the thermodynamic potential (1), one finds the equilibrium value of the order parameter:

$$\psi_0^2 = (1/2d) \left( \sqrt{b^2 - 4ad} - b \right). \tag{4}$$

Substitution of this expression into formula (3) gives an equation of the first-order transition line in terms of the coefficients a, b and d:

$$3b^2(P,T) = 16a(P,T)d(P,T).$$
 (5)

We assume that d(P,T) > 0. One can see then, from the above formula, that on the line of first-order transitions, a(P,T) > 0. The line a(P,T) = 0 for b(P,T) < 0 has the meaning of a boundary of stability of the normal phase, or a limit of overcooling. The limit of overheating of the superconducting phase is a line:  $a = b^2/4d$ . The line of transition in a superconducting state now consists of two parts: a(P,T) = 0 for b > 0 and the line given by equation (5) for b < 0. These parts meet each other at the TCP with a continuous tangent. On crossing the line (5), the order parameter jumps from zero to a finite value:

$$|\psi|^2 = -3b/4d.$$
 (6)

Simultaneously, the entropy and the volume jump:

$$S_{\rm s} - S_{\rm n} = (3b/4d)(\partial a/\partial T)_P \qquad V_{\rm s} - V_{\rm n} = (\mathrm{d}T_{\rm c}/\mathrm{d}P)(S_{\rm s} - S_{\rm n}). \tag{7}$$

Both jumps vanish at the TCP. In a region with b > 0, both the entropy and volume are continuous, but the specific heat of the superconducting phase develops a singularity  $C_{\rm p} \sim (T_{\rm t} - T)^{-1/2}$  when the TCP is approached from a region with b > 0.

We have summarized above some of the known general properties of any phase transition in the vicinity of a tricritical point [8]. Specifics of a superconductor manifest themselves when the transition takes place in a magnetic field. To begin with, we define the thermodynamic critical field  $H_{\rm cm}$ , i.e. the critical field corresponding to a transition into the Meissner phase with a complete expulsion of the magnetic field from a bulk superconductor. We assume, as usual, that the sample is a long cylinder with the axis oriented parallel to the field. In the presence of a field, one has to substitute  $\phi_n - H^2/8\pi$  instead of  $\phi_n$  into the condition of thermodynamic equilibrium (3). For the thermodynamic potential (1), this gives:

$$a + b|\psi|^2 + d|\psi|^4 = 0 \tag{8}$$

$$a|\psi|^{2} + (b/2)|\psi|^{2} + (d/3)|\psi|^{6} = -H^{2}/8\pi.$$
(9)

After eliminating  $|\psi|^2$  from these equations, we arrive at an expression for  $H_{cm}$  in terms of the coefficients a, b and d:

$$H_{\rm cm}^2 = (\pi/3d^2) \left(\sqrt{b^2 - 4ad} - b\right)^2 \left(2\sqrt{b^2 - 4ad} + b\right). \tag{10}$$

The critical field becomes zero when one of the last two brackets in this formula is zero. At b > 0, the second bracket turns to zero at a = 0, i.e. on the line of second-order transitions. In the vicinity of this line, when  $4|a|d \ll b^2$ , formula (10) gives the usual expression for the critical field  $H_{cm}^2 = 4\pi a^2/b$ . In this case  $H_{cm}$  tends to zero linearly as  $(T_c - T)$ , when T approaches  $T_c$ . At b < 0, the field  $H_{cm}$  vanishes, together with the third bracket in formula (10) on the line of first-order transitions, defined by equation (5). In the vicinity of this line  $H_{cm}^2 = 6\pi(a|b|/d)(T_{cl} - T)$ , where  $T_{cl}$  is the temperature of the first-order transition in a zero field. In this case,  $H_{cm}$  tends to zero as the square root of  $(T_{cl} - T)$ , in agreement with the general relation  $S_s - S_n = (1/8\pi)dH_{cm}^2/dT$  and formula (7).

For usual superconductors,  $H_{cm}$  is the true critical field only if the superconductor is of type I. The criterion for the assignment to type I is formulated in terms of the parameter of Ginzburg and Landau which, in this case, has the form  $\kappa = (mc/e\hbar)(b/2\pi)^{1/2}$ , and the criterion is  $\kappa < 1/\sqrt{2}$ . Such a criterion, for obvious reasons, cannot be applied when b is negative, and in this case the critical field has to be found anew. This question exists not just for negative b. The TCP creates in its vicinity a region where the sixth-order terms in expansion (1) are important. This region is defined by the condition  $b^2 \leq 4|a|d$ , taken together with a general condition of applicability of the Ginzburg and Landau theory  $(T_c - T)/T_c \ll 1$ , and it includes positive b as well. Such a region can exist even if a TCP is only 'virtual', i.e. b is positive, but the above-mentioned conditions are met. To make a clear distinction in what follows we will denote as 'usual' those superconductors for which b is positive and the strong inequality  $b^2 \gg 4|a|d$  holds in a region of applicability of the theory of Ginzburg and Landau.

The equations of Ginzburg and Landau are necessary for finding the critical magnetic field, and in the next section we discuss the changes which have to be introduced in these equations for a superconductor with a TCP.

### 3. The equations of Ginzburg and Landau

Following the usual procedure of derivation of the Ginzburg-Landau equations, we write down the free energy of a superconductor in the form

$$\mathcal{F}_{s} = \mathcal{F}_{n0} + \int \left[ \frac{B^{2}}{8\pi} + \frac{\hbar^{2}}{4m} \left| \left( \nabla - \frac{2ie}{\hbar c} A \right) \psi \right|^{2} + F_{s} \right] dv.$$
(11)

Here,  $\mathcal{F}_{n0}$  is the free energy in the normal state, B (= curl A) is a magnetic field, e,  $\hbar$ , c and m are universal constants, and a possible anisotropy of the gradient term in the energy is not taken into account. The difference with respect to the usual case, is that the sixth-order terms are kept in the density of the bulk free energy:

$$F_{\rm s} = a|\psi|^2 + \frac{1}{2}b|\psi|^4 + \frac{1}{3}d|\psi|^6.$$
<sup>(12)</sup>

By variation of this functional over  $\psi^*$  and the vector potential A one obtains two equations:

$$(1/4m)\left(-i\hbar\nabla - \frac{2e}{c}A\right)^2\psi + \partial F_s/\partial\psi^* = 0$$
(13)

$$\operatorname{curl}\,\operatorname{curl}\,\boldsymbol{A} = -\frac{4\pi}{c} \left[ \frac{\mathrm{i}e\hbar}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) + \frac{2e^2}{mc} |\psi|^2 \boldsymbol{A} \right]. \tag{14}$$

The boundary conditions for equations (13) and (14) remain the same as in the usual case.

The equations look simpler when dimensionless variables are introduced. Following Abrikosov [9] we denote these variables by primes:  $\psi' = \psi/\psi_0$ , where  $\psi_0$  is the equilibrium value of the order parameter, defined by formula (4), and  $r' = r/\delta$ , where  $\delta$  is a penetration depth, defined as

$$\delta^2 = mc^2 / 8\pi e^2 \psi_0^2. \tag{15}$$

Another characteristic length in the problem is the correlation radius for fluctuations of the order parameter  $\xi$ . Following the standard theory of fluctuations [8], we obtain for this radius

$$\xi^2 = -\hbar^2 / 4m(2a + b\psi_0^2). \tag{16}$$

The ratio of the two lengths defines the parameter of Ginzburg and Landau:

$$\kappa^2 = (\delta/\xi)^2 = (1/2\pi)(mc/e\hbar)^2 \sqrt{b^2 - 4ad} = (1/2b_0)\sqrt{b^2 - 4ad}.$$
(17)

The notation  $b_0 = \pi (e\hbar/mc)^2$  is introduced here for brevity. The characteristic field  $H_0$  is defined as  $H_0 = \hbar c/2e\xi\delta$  (cf [10]). This field does not coincide with  $H_{cm}$  and is not proportional to it. Only in the limit  $ad/b^2 \rightarrow 0$  does  $H_0$  tend to  $H_{cm}\sqrt{2}$ . With the use of the field  $H_0$ , further dimensionless quantities can be introduced:

$$B' = B/H_0$$
  $A' = A/H_0\delta$   $F'_s = (8\pi/H_0^2)F_s$ .

In comparison with the usual superconductors,  $F_s$  contains an additional parameter the coefficient d. This means that when dimensionless units are introduced, an additional dimensionless parameter will enter the Ginzburg-Landau equations besides  $\kappa$ . It turns out to be convenient to introduce, as such a parameter, the combination

$$\theta = b/\sqrt{b^2 - 4ad} = \frac{b}{2b_0\kappa^2}.$$
(18)

In terms of  $\theta$ , the free energy density can be rewritten as

$$F'_{\rm s} = -[(1+\theta)/2]|\psi'|^2 + (\theta/2)|\psi'|^4 + [(1-\theta)/6]|\psi'|^6.$$
(19)

One can see from definition (18) that within the domain of existence of a superconducting phase,  $\theta$  varies in the interval  $-2 < \theta < 1$ ;  $\theta = 1$  everywhere on

the line of second-order transitions, and  $\theta = -2$  on the line of first-order transitions. In the new variables, equations (13) and (14) assume the following form:

$$(-(\mathbf{i}/\kappa)\nabla' - \mathbf{A}')^2\psi' + \partial F'_{\mathbf{s}}/\partial\psi'^* = 0$$
<sup>(20)</sup>

curl curl 
$$A' = -(i/2\kappa)(\psi'^* \nabla \psi' - \psi' \nabla \psi'^*) - |\psi'|^2 A'.$$
 (21)

At  $\theta = 1$ , the expression for the free energy density (19) acquires its usual form (cf [9]).

For the free energy in dimensionless units, we obtain

$$\mathcal{F}_{s} = \mathcal{F}_{u0} + \frac{H_{0}^{2}}{8\pi} \delta^{3} \int \left[ B^{\prime 2} + \left| \left( -\frac{i\nabla^{\prime}}{\kappa} - A^{\prime} \right) \psi^{\prime} \right|^{2} + F_{s}^{\prime} \right] dv^{\prime}.$$
(22)

When  $\psi$  and A satisfy equations (20) and (21) this expression can be transformed in such a way that the gradient term disappears:

$$\mathcal{F}_{\rm s} = \mathcal{F}_{\rm n0} + \frac{H_0^2}{8\pi} \delta^3 \int \left[ B^{\prime 2} + F_{\rm s}^\prime - |\psi^\prime|^2 \frac{\partial F_{\rm s}^\prime}{\partial |\psi^\prime|^2} \right] \,\mathrm{d}v^\prime. \tag{23}$$

The contribution from the surface term to the free energy was neglected in transforming from (22) to (23).

In a summary of this section, we can say that for a proper description of a superconductor with a TCP it is necessary to introduce one more parameter in the Ginzburg-Landau theory. The usual situation corresponds to one particular value of this parameter.

# 4. The critical field

The thermodynamic critical field, which was discussed in section 2, is one of two characteristic fields for usual superconductors. The other field is the boundary of stability of the normal phase— $H_{c2}$ . The expression for  $H_{c2}$  does not depend on higher-order terms in expansion (1), and it is given by the usual formula:

$$H_{c2} = -(2mc/e\hbar)a. \tag{24}$$

It was shown by Abrikosov [11] that for usual superconductors, when  $\kappa > 1/\sqrt{2}$ ,  $H_{c2}$  is greater than  $H_{cm}$  for all temperatures below  $T_c$ , and the transition into a superconducting state takes place exactly at  $H = H_{c2}(T)$ . The appearing state (the mixed state) is periodic in space and a magnetic field penetrates into the superconductor in the form of quantized flux lines. The average value of the order parameter tends to zero when H approaches  $H_{c2}$  from below, i.e. a transition between the normal and the mixed state is of second order. It will be shown in this section that, for a superconductor with a TCP, the effect of a magnetic field on a superconducting transition, in comparison with the usual superconductors, has two new important features:

(i) transition into the mixed state can be of first order and can take place at  $H > H_{c2}$ ;

(ii) the lines  $H = H_{cm}(T)$  and  $H = H_{c2}(T)$  in the (T, H) plane intersect at a finite field, unless  $\kappa < 1/\sqrt{2}$  everywhere in the domain of superconductivity.

To prove the first statement, one has to apply the arguments of Abrikosov to equations (20) and (21). Following the derivation given in [9], we arrive at the following equation for the averaged value of  $|\psi'|^2$ :

$$(1/\kappa)(H' - H'_{c2})\overline{|\psi'|^2} + (\theta - 1/2\kappa^2)\beta_A \left(\overline{|\psi'|^2}\right)^2 = 0$$
(25)

where  $\beta_A$  is the ratio  $|\psi'|^4/(|\psi'|^2)^2$ . This ratio is of order unity and is different for different vortex lattices. The sign of the coefficient in front of the quartic term in equation (25) defines the character of the transition in the mixed state. Using definitions (17) and (18) we can rewrite this coefficient in the following form:

$$\theta - 1/2\kappa^2 = (b - b_0)/\sqrt{b^2 - 4ad}.$$
 (26)

When  $b > b_0$ , the familiar case is obtained: equation (25) has a finite solution for  $H < H_{c2}$ :  $|\psi|^2 \sim (H_{c2} - H)$ , and the transition is of second order. At  $b < b_0$ , a transition into the mixed state is of first order, and takes place at  $H > H_{co}$ . To find the value of the critical field, one would have to keep, in the equation for  $|\psi|^2$ , terms up to the sixth order. Such an analysis has not yet been done. The situation at  $b = b_0$  is marginal. Let us consider first the case when  $\theta = 1$ , and the superconductor is usual. In this case the condition  $b = b_0$  is equivalent to  $\kappa = 1/\sqrt{2}$ : this is simultaneously met for all points on the line  $H_c(T)$  and it signals a transition of a superconductor from type II to type I. Such a behaviour is due to the fact that in the usual situation b is treated as a constant. An account of its temperature dependence would be consistent only if the sixth-order terms in the energy were kept. In the vicinity of the TCP, when the sixth-order terms have to be taken into account, the temperature dependence of b becomes essential. The condition  $b = b_0$  defines a line in the (T, P) plane (cf figure 1). Depending on the slope of this line different situations may arise. Of particular interest is the possibility represented in figure 1, i.e. when the angle between the lines  $b(P,T) = b_0$  and a(P,T) = 0 at the point of their intersection is small. With increasing magnetic field, the transition point moves from the line a(P,T) = 0 to lower temperatures. At a certain field  $H_t$ , it can cross the line  $b(P,T) = b_0$ . This point will be tricritical on the line  $H_c(T)$ . At  $H < H_t$ , the transition is of first order and at  $H > H_{t}$ , of second. From general arguments [8], which apply to all TCPs, one can conclude that there must be no change in the slope of the curve  $H_c(T)$  at the TCP; only the second derivative of  $H_c$  on T is discontinuous. If such a crossing does not occur, the transition remains of first or of second order, down to the lowest temperatures, depending on the value of b on the line a(P,T) = 0 at a given pressure. These arguments have exact meaning only within the region of applicability of the Ginzburg-Landau theory, but they can be used as a qualitative guide beyond this region.

To prove that the lines  $H_{cm}(T)$  and  $H_{c2}(T)$  intersect, it is sufficient to find a point of their intersection. This can be done easily when both fields are expressed in terms of  $\kappa^2$  and  $\theta$ . It is convenient also to introduce into these expressions, instead of the coefficient d, a term proportional to  $H_d$ , which has the dimensionality of a magnetic field, and is defined as

$$H_{\rm d}^2 = (8\pi/3)b_0^3/d^2. \tag{27}$$





Figure 1. The phase diagram of a superconductor with a TCP. The full curve represents the first-order transition, the broken curve that of second order. On the curve MM' the condition  $b(P, T) = b_0$  is met.

Figure 2. The (T, H) phase diagram of a superconductor with a TCP. The full curve represents the first-order transition. *M* is the TCP. At the point  $\sigma$  the surface energy between the normal and superconducting phases turns to zero. The critical fields  $H_{\rm cm}$ ,  $H_{\rm c2}$  and  $H_{\rm c1}$  have their usual meanings. Below the line  $H_{\rm c1}$  the superconductor is in the Meissner phase; above it, it is in the mixed state.

After substitution of (17), (18) and (27) in the formulae (10) and (24), we obtain

$$H_{\rm cm} = H_{\rm d} \kappa^3 (1-\theta) \sqrt{2+\theta} \tag{28}$$

$$H_{c2} = H_{\rm d} \sqrt{\frac{3}{2}} \kappa^4 (1 - \theta^2). \tag{29}$$

These equations are easily solved with respect to  $\kappa^2$  and the ratio  $H_i/H_d$  where  $H_i$  is the field at the intersection point:

$$\kappa^2 = \frac{2}{3}(2+\theta)/(1+\theta)^2 \qquad H_i/H_d = \left(\frac{2}{3}\right)^{3/2}(2+\theta)^2(1-\theta)/(1+\theta)^3$$

For any  $\kappa > 1/\sqrt{2}$  there exists a  $\theta$  satisfying the first of these equations and belonging to the interval  $-1 < \theta < 1$ . When  $\theta$  is known, we can substitute it into the second equation and find the corresponding field  $H_i$ .

Now we are able to describe the full dependence of the critical field on temperature for a superconductor with a TCP (cf figure 2). At zero field, the transition into the superconducting state is of first order and it takes place at a > 0. The only critical field which exists at a > 0 is  $H_{\rm cm}$ . This means that, for small fields,  $H_c(T)$  coincides with  $H_{\rm cm}(T)$ . The surface energy between the normal and superconducting phases  $\sigma_{\rm ns}$ , at zero field, is obviously positive. This means that, for small fields, the formation of vortices is disadvantageous and the superconducting state is formed as the Meissner phase even though the parameter  $\kappa$  in that region can be much greater than unity. When the field increases, the surface energy decreases. Calculation of

the surface energy, which will be published separately [12], shows that when the lines  $H_{c2}(T)$  and  $H_{cm}(T)$  intersect this energy changes sign at a certain point  $\sigma$ :  $(T_{\sigma}, H_{\sigma})$  on the line  $H_{cm}(T)$  before its intersection with  $H_{c2}(T)$ . At fields  $H > H_{\sigma}$ , creation of vortices becomes advantageous and the superconducting phase should form in the mixed state. Since, at  $H > H_{\sigma}$ , the energy of the mixed state is smaller than the energy of the Meissner phase at the same field and temperature, the line of the phase transition  $H_c(T)$ , starting from the point  $\sigma$ , is deflected from  $H_{cm}(T)$  to higher fields (or temperatures). The normal phase is still stable in this region of the (T, H) plane and the transition into the mixed state is of first order.

According to the above discussion, there are two possibilities for the behaviour of  $H_c(T)$  at even higher fields. Either  $H_c(T)$  joins the line  $H_{c2}(T)$  at a TCP and at higher fields it coincides with  $H_{c2}$ , or the transition remains of first order down to zero temperature.

We conclude that for a superconductor with a TCP the line  $H = H_c(T)$  can contain three segments:

(1) a first-order transition segment  $H = H_{cm}(T)$  for  $0 < H < H_{\sigma}$ ;

(2) a first-order transition segment  $H = H_c(T)$ ,  $H_c(T) > H_{c2}$ ,  $H_{cm}$  for  $H_{\sigma} < H < H_t$ ; and

(3) a second-order transition segment  $H = H_{c2}(T)$  for  $H > H_t$ .

In the region below  $H_c(T)$  there are at least two different superconducting states—the Meissner phase and the mixed state. These states are separated by the line  $H_{cl}(T)$ , which must branch from  $H_{cm}(T)$  near the point  $\sigma$ . This is the lower critical field, at which formation of the flux lines becomes advantageous. The behaviour of this line is similar to that for usual superconductors. There is, however, a qualitative difference: for superconductors with a TCP the line  $H_{cl}$  starts at a finite field. This property can be used for experimental identification of a superconductor with a TCP.

A further subdivision of the mixed state is possible. For usual superconductors the only parameter characterizing a lattice in the vicinity of  $H_{c2}$  is  $\beta_A$ , and minimum of  $\beta_A$  is a minimum of energy [9]. Explicit minimization shows that the triangular lattice is the most favourable in this case [10]. When higher-order terms are essential, the new characteristics of a lattice will enter the problem, e.g. as a ratio  $|\psi|^6/(|\psi|^2)^3$ . The known arguments do not apply in this case and an equilibrium lattice has to be found anew. With respect to the phase diagram of a superconductor with a TCP this means that in a region  $H \gg H_t$ , when the transition is of second order, we can use known results and claim that the equilibrium lattice at  $H < H_t$ . One can expect, in principle, a transition between different lattices in a region  $H \sim H_t$ . No definite statement can be made until an analysis of energies of different lattices for the case  $b < b_0$  is performed.

### 5. Application to UPt<sub>3</sub>

The theory developed in the previous sections, makes it possible to suggest a new interpretation of the complex phase diagram of UPt<sub>3</sub>, both in (T, P) and in (T, H) coordinates. We start with the (T, P) diagram, although the magnetic diagram was investigated earlier [13]. The effects of hydrostatic pressure [14] and uniaxial stress

[15] on the superconducting transition in  $UPt_3$  have been investigated experimentally. Since the above theory was developed for an isotopic case and formulated in terms of pressure, we discuss here only the hydrostatic pressure data. There is no contradiction with the uniaxial stress data, but the necessary modification of the theory, although straightforward, leads to additional complications.

At pressures above  $\sim 4$  kbar, a single clear jump in the specific heat is observed at the superconducting transition. At lower pressures an additional feature appears on the temperature dependence of specific heat and, below  $\sim 2$  kbar, two jumps can be resolved. Such behaviour of the specific heat is considered to be evidence for splitting of the superconducting transition and the occurrence of another superconducting phase. Different interpretations of these data are possible. We assume that, in the vicinity of the transition at normal pressure, the coefficient b in expansion (1) for UPt<sub>3</sub> is negative. With increasing pressure, b increases until it turns to zero at a point  $(T_t, P_t)$ , which, as a result, is tricritical. We identify this point with the point where two jumps in the specific heat merge. From the data of [14]  $T_{t} = 0.42$  K and  $P_{\rm t} = 3.7$  kbar. At pressures below  $P_{\rm t}$ , the superconducting transition is of first order. The jumps in the volume and the entropy, associated with the transition, can produce stresses in a solid sample. Because of the stresses, the transition temperature will broaden into a coexistence interval  $\Delta T$ . Within this interval, the superconducting and normal regions coexist in a sample. The width of the interval and the particular dependence of specific heat on temperature depend on the experimental conditions. A physically significant quantity is the overall change in entropy. It is not easy to extract this change from the existing data because of the complicated structure of the observed curves. The situation is more favourable for a jump in the volume. One can use for the estimation of this jump the data on a thermal expansion coefficient of UPt<sub>3</sub> [16]. Integration of the temperature dependence of the thermal expansion coefficient, represented in figure 2 of [16], shows a clear change of the relative size of the sample in the direction of the c axis at the phase transition. This change can roughly be estimated as being  $\Delta L/L_c \sim 10^{-8}$ . With formulae (7), the combination of coefficients  $\alpha b/d$  could be extracted from these data. Unfortunately an ambiguity introduced by extrapolations from the regions remote from the transition makes this estimate rather crude.

The phase diagram in the (T, H) plane, which emerges from the thermodynamic data at normal pressure [13], looks similar to that in the (T, P) plane. Two jumps are observed in the temperature dependence of the specific heat at low fields. When the field increases, the jumps merge into one at a certain field  $H_t$ , which is of the order of 1 T Within the suggested scheme, this diagram has the same interpretation as the (T, P) diagram. At zero field, according to the main assumption, the transition is of first order. Upon increasing H, whereby T decreases, and remaining within the  $b < b_0$  limitation, the transition remains of first order until the temperature  $T_M$  is reached, where b becomes equal to  $b_0$ . According to the present scheme, this is the temperature at which two singularities in the specific heat merge. The critical field corresponding to  $T_M$  is, according to (24):

$$H_{\rm M} = -2\left(\sqrt{\pi/b_0}\right)a(P_0,T_{\rm M}).$$

At higher fields (and lower temperatures) the transition is of second order and the point  $(T_M, H_M)$  is tricritical. For reasons which have already been discussed, the

In the vicinity of the TCP, all properties of the superconducting phase can be expressed in terms of the four derivatives  $\partial a/\partial P$ ,  $\partial a/\partial T$ ,  $\partial b/\partial P$ ,  $\partial b/\partial T$  taken at the TCP and the coefficient d, which may be considered as a constant as well. The available data are not yet sufficient to extract all these coefficients.

Acoustic measurements [17, 18] confirm the splitting of the superconducting transition and reveal two more transition lines in the superconducting region. One is the  $H_{cl}$  line, the other line branches from  $H_c(T)$ , approximately at the level of the point M. Within the present scheme this could be a change of structure of the vortex lattice. This observation calls for a further theoretical investigation of the mixed state in superconductors with a TCP.

There is no direct conflict between the experimental data on phase diagrams of UPt<sub>3</sub> and the suggested scheme of their interpretation. This scheme is also free from certain shortcomings of the previously suggested schemes. In particular, the field  $H_t$  need not depend strongly on its orientation with respect to the crystallographic axes, and the observed irreversibility of the penetration of the magnetic field [7] fits the idea of a first-order transition. There are further qualitative features, which can be tested experimentally, such as a hysteresis at the first-order transition line in the (T, P) plane and a singularity of specific heat at the TCP. One can also think of a direct observation of a phase separation at the first-order transition. An investigation of the phase diagram, whereby both pressure and magnetic field can be varied, would be of considerable assistance. In view of the implications, which were discussed in the introduction, an experimental check of the suggested scheme would be of importance for understanding the phenomena of superconductivity in heavy-fermion materials.

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