ture with both increasing and decreasing stress. The transition temperature at a given stress varied by less than 0.4 mK. A similar Mylar puller was used by Davis, Skove, and Stillwell[18] and gave results for tin which were consistent with Grenier's[19] work with bulk tin single crystals. The different methods of calibrating the thermometer were consistent within 1 mK from 2.5 to 4.2°K, and changes in temperature in the region around 3.4°K were consistent to within 0.2 mK.

There seems to be no simple explanation for the factor of 2 difference between these results and those of Rohrer and of Collins *et al.* The thermodynamic reversibility of the transition is well established. Whiskers of Sn give results that are consistent with those of bulk Sn, and thus there is no reason to suppose that whiskers do not act as bulk material does. Indeed, even in the smallest whiskers ($\sim 0.1\ \mu$ diameter) fluctuation effects are negligible.[20] The extrapolation procedure used in finding the ratio $(l_s-l_n)/H_c$ at T_c (where both l_s-l_n and H_c are zero) does not appear to give difficulties. There may be others difficulties in the measurement of $(l_s-l_n)/H_c$, since Collins *et al.* and Rohrer find values of (l_s-l_n) with differing signs for rods whose axes lie in the base plane.

[18] J. H. Davis, M. J. Skove, and E. P. Stillwell, Solid State Commun. **4**, 597 (1966).

[19] C. Grenier, Compt. Rend. **238**, 2300 (1954).

[20] W. W. Webb and R. J. Warburton, Phys. Rev. Letters **20**, 461 (1968).

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Observed Large Deviation of the Superconductive Critical-Field Ratio H_{c3}/H_{c2} from the Existing Theories near T_c†

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The ratio H_{c3}/H_{c2} is calculated in the presence of a phonon-mediated interaction which is slightly depressed in a surface layer. It is shown that if the surface layer has a thickness of order ξ_0, then this ratio will drop rapidly to unity as the transition temperature is approached from below. This result is in good agreement with the recent observation by Ostenson and Finnemore, who reported that for temperatures very close to T_c, the ratio H_{c3}/H_{c2} falls far below the factor 1.7 of Saint-James and de Gennes. The present paper gives a mean-field-theory explanation of this phenomenon.

I. INTRODUCTION

BY solving the linearized Ginzburg-Landau (GL) equation[1] in a half space, with the boundary condition that the solution should have a vanishing slope at the surface, Saint-James and de Gennes[2] first predicted that the ratio H_{c3}/H_{c2} for a superconductor should always be equal to 1.695, independent of many properties of the sample. The surface nucleation critical field H_{c3} is the maximum magnetic field that can be applied, parallel to one of the surfaces of a bulk sample, without suppressing all superconducting properties of the sample. It also marks the first appearance of a thin superconducting sheath near the sample surface, which is parallel to an applied field, when the applied field is lowered continuously from above. The upper critical field for the vortex state H_{c2} is also called the bulk nucleation critical field, because it also marks the onset of a localized superconducting region deep inside a bulk sample, at decreasing field. For pure materials, Saint-James and de Gennes's prediction is valid only in a narrow temperature region near the transition temperature T_c, satisfying the criterion $T_c-T\ll T_c$, which is commonly referred to as the GL region. Ebneth and Tewordt,[3] and Lüders[4] subsequently extended the work of Ref. 2 to just below the GL region and found a correction term 1.041 $(1-t)$, where $t\equiv T/T_c$, to the ratio H_{c3}/H_{c2} for a sample with a specular surface. Hu and Korenman[5] then succeeded in showing that the expansion parameter near T_c is actually $(1-t)^{1/2}$, and in addition to reproducing the above conclusions, have found that the next order term is $-0.978\ (1-t)^{3/2}$. As $T\rightarrow 0$°K, the ratio was also found to approach a value equal to or larger than 1.925 with vanishing slope. The following interpolation

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[1] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

[2] D. Saint-James and P.-G. de Gennes, Phys. Letters **7**, 306 (1963).

[3] G. Ebneth and L. Tewordt, Z. Physik **185**, 421 (1965).

[4] G. Lüders, Z. Physik **202**, 8 (1967). Notice that the value of a constant C defined in this paper has later been changed from 1.36 to 0.762. [G. Lüders and K.-D. Usadel, Z. Physik **222**, 358 (1969); see also, K.-D. Usadel and M. Schmidt, Z. Physik **221**, 35 (1969)].

[5] C.-R. Hu and V. Korenman, Phys. Rev. **178**, 684 (1969), (to be referred to as I in the present paper); **185**, 672 (1969) (to be referred to as II in the present paper).

formula was proposed to cover the whole temperature range below T_c:

$$H_{c3}(T)/H_{c2}(T)=1.695[1+0.614(1-t)-0.577(1-t)^{3/2}-0.007(1-t)^2+0.106(1-t)^{5/2}]. \quad (1)$$

Evidence was given that this formula is at least semiquantitatively correct for temperatures not too close to T_c. This predicted temperature dependence of H_{c3}/H_{c2} shall be referred to as the "simple picture."

Ostenson and Finnemore[6] reported very recently that at least for the two pure Nb samples they investigated, the critical-field ratio deviated strongly away from the simple picture as $t>0.85$, and dropped exponentially to the neighborhood of unity as T approached T_c. They emphasized that the simple picture is a mean-field-theoretical prediction, and attributed the observed deviation to the effect of critical fluctuations in the surface sheath. There seem to be several arguments against such an interpretation: (1) It is well known[7] that the critical region for a pure bulk superconductor is extremely small because of the large zero-temperature (or *BCS*[8]) coherence length ξ_0 involved. In fact, when the Ginzburg criterion[9] is applied directly to pure Nb, using the data supplied by Finnemore *et al.*,[10] one immediately finds that its critical region ϵ_c is $<10^{-12}$, where $\epsilon\equiv 1-t$. For amorphous materials with much reduced zero-temperature coherence lengths, the critical region could be much larger,[11] but this has no bearing on Ostenson and Finnemore's experiment, as they used very pure material. Now, since fluctuations in the surface sheath are governed by the same coherence length as in a bulk superconductor, and since the thickness of a surface sheath is always of the same order as the finite-temperature coherence length $\xi(T)$, this sample should not be regarded as a thin film so far as the effects of critical fluctuations are concerned.[12] It is therefore hard to conceive of an enhancement factor to ϵ_c for surface superconductors of the order of 10^{11}, as would be needed to explain Ostenson and Finnemore's experiment. (2) From the ways H_{c3} and H_{c2} are defined,[13] as they are briefly restated in the beginning of this paper, one would imagine that bulk nucleation and surface nucleation are essentially similar proceses, so that if critical fluctuations are important to H_{c3}, they should also be important to H_{c2}. The effects may not cancel each other in the ratio H_{c3}/H_{c2}, but an effect should be observed in the ratio H_{c1}/H_{c2}, where H_{c1} is the lower critical field of the vortex state. This latter effect was not, however, observed according to Ref. 6. (3) It was emphasized in Ref. 6 that for surface superconductivity, the total change in the free energy due to the phase transition is small, as the contributing volume occupied by the surface sheath is small. What has not been pointed out is the fact that for $H\approx H_{c3}>H_{c2}$, the main bulk of the system is free from critical fluctuations, so that the total effect of the critical fluctuations ought to have been reduced by the same factor. Thus in this aspect, surface superconductivity seems to have no advantage over bulk superconductivity. (4) It was further argued in Ref. 6 that when the width of the surface sheath grew larger as T approached T_c, the available free energy per unit superconducting volume became smaller and smaller. It was then assumed that the probability for a region of the surface to fluctuate into a normal state was exponential in the negative of this free-energy density, so that fluctuation effects could be exponentially larger for T closer to T_c. This conclusion sounds very reasonable, but the argument could also lead to the conclusion that fluctuation effects would be smaller if the growing width of the surface sheath were limited by the second surface of a thin superconducting film. This seems to contradict the currently accepted conclusions about the effects of sample size on critical fluctuations.[12]

Although these arguments may not suffice to rule out the critical fluctuations as a possible cause of the observed effect, they at least suggest that the alternative possibility of a mean-field–theoretic explanation may also be worth an examination. This idea becomes even more attractive in that one can find at least one example in the realm of mean field theory where a small perturbation to a superconducting system can actually produce an effect very similar to what Ostenson and Finnemore has observed.

Section II contains one such example. Section III is devoted to demonstrating that Ostenson and Finnemore's observation can be well-fitted by the present theory. At the end of Sec. III, we shall also point out briefly several other possibilities within the context of a mean field theory which could produce essentially the same effect.

II. MEAN-FIELD-THEORETIC MODEL

Since the purpose of this section is to present an example in the realm of mean field theory which could produce the effect observed by Ostenson and Finnemore, it is assumed that all fluctuation effects are completely negligible. Then the behavior of a superconductor at all $T\leqslant T_c$ can be fully described by the BCS theory,[8] or

[6] J. E. Ostenson and D. K. Finnemore, Phys. Rev. Letters **22**, 188 (1969).
[7] See, for example, L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967).
[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[9] V. L. Ginzburg, Fiz. Tverd. Tela. **2**, 2031 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1824 (1960)]; A. P. Levanyuk, Zh. Eksperim. i Teor. Fiz. **36**, 810 (1959) [English transl.: Soviet Phys.—JETP **9**, 571 (1959)].
[10] D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, Phys. Rev. **149**, 231 (1966).
[11] See, for example, J. S. Shier and D. M. Ginsberg, Phys. Rev. **147**, 384 (1966); R. E. Glover, III, Phys. Letters **25A**, 542 (1967).
[12] See the discussions on this point by L. P. Kadanoff and G. Laramore, Phys. Rev. **175**, 579 (1968).
[13] See, for example, P.-G. de Gennes, *Superconductivity of Metals and Alloys*, transl. by P. A. Pincus (W. A. Benjamin, Inc., New York, 1966). See also Refs. 2 and 5.

its generalization to cover nonhomogeneous situations, the Gor'kov theory.[14]

Consider a semi-infinite pure superconducting system occupying the region $z>0$, characterized by a space-dependent interaction $V(z)$.[15] In particular, let us consider the case when $V(z)=\lambda+V_1(z)$, with $V_1(z)\equiv\lambda_1\theta(D-z)$, where $\theta(x)$ is the unit step function. We shall assume $\lambda<0$, so that the main bulk can become superconducting, and $|\lambda_1|\ll|\lambda|$, so that only effects of first order in λ_1/λ need be considered. Let L denote the width of the surface sheath, whose exact definition will be given later. It is expected that $L\propto\xi_0(1-t)^{-1/2}$, which can be larger or smaller than D depending on the sample temperature. Because of this, and for another reason which can only be made clear later, a proper discussion requires that we divide the temperature range between absolute zero and T_c into three nonoverlapping regions.

Region A

This region is defined by $D>L$ which is expected to cover the temperature range between absolute zero and a maximum temperature below T_c, the exact definition of which will become clear later. In this region, the surface sheath sees essentially a homogeneous system of interaction strength $\lambda+\lambda_1$, so that the measured critical-field ratio must be $H_{c3}(\lambda+\lambda_1)/H_{c2}(\lambda)\equiv C(T)H_{c2}(\lambda+\lambda_1)/H_{c2}(\lambda)$, where $C(T)$ is the simple picture value of the ratio Eq. (1). If we approximate $H_{c2}(T)$ by $-[dH_{c2}(t)/dt]_{t=1}(1-t)$ and observe that the coefficient of $(1-t)$ will depend on the interaction parameter, being proportional to T_c^2,[13] we then obtain

$$\frac{H_{c3}(\lambda+\lambda_1)}{H_{c2}(\lambda)}\cong C(T)\left(2\frac{\delta T_c}{T_c}+\frac{1+\delta T_c/T_c-t}{(1+\delta T_c/T_c)(1-t)}\right).$$

Following Ostenson and Finnemore, δh is defined to be the difference between the simple picture value and the actually measured value of this ratio. Using the BCS formula[8] for $T_c(\lambda)$ to find $\delta T_c/T_c=[N(0)|\lambda|]^{-1}\times(\lambda_1/\lambda)$, where $N(0)$ is the electron density of states at the Fermi surface, we conclude that[16]

$$\delta h\cong[C(T)/C(T_c)]Z[(2-t)/(1-t)],\qquad(2)$$

where $Z=1.695[N(0)|\lambda|]^{-1}(-\lambda_1/\lambda)$.

In the following, we shall only consider the case $\lambda_1/\lambda<0$, so that the phonon-mediated interaction is weaker near the surface. Equation (2) then implies that the critical-field ratio will drop below the simple picture value, especially near T_c as observed by Ostenson and Finnemore, except possibly for an incorrect temperature dependence. But as T moves close enough to T_c, it must enter into the next temperature region.

Region B

This region is for the moment defined only by $L(T)>D$. In this region, one might expect the effective additional interaction component λ_1 to be reduced by a factor D/L, if it is the *average* $V(\mathbf{r})$ within the surface sheath which determines δh. We can make further progress only if region B already lies entirely within the GL region. We then expect $L\propto\xi_0\epsilon^{-1/2}$, so that

$$\delta h=Z'\epsilon^{-1/2},\qquad(3)$$

where $Z'=ZD_{\text{eff}}/\xi_0$. So far we only know that $D_{\text{eff}}\equiv D\xi_0/L\epsilon^{1/2}\propto D$.

To find D_{eff}, an exact defintion of L is needed. Besides, Eq. (3) cannot be correct in the extreme neighborhood of T_c as it can make the critical-field ratio <1 and even negative. To resolve these two points, we turn to a different approach.

The linearized Gor'kov gap equation[14] for the pair wave function $\Delta(\mathbf{r})$ is

$$\Delta(\mathbf{r})=\left[\frac{V(z)}{\lambda}\right]\int K(\mathbf{r},\mathbf{r}')\Delta(\mathbf{r}')d\mathbf{r}',\qquad(4)$$

where the kernel $K(\mathbf{r},\mathbf{r}')$ has been given in (I-22).[5] We shall solve (4) by a method developed in Paper II.[5] In particular, we define $\xi_0(T)=v_F/2\pi T$, $\xi_0=\xi_0(T_c)$, $\xi_H=(2eH)^{1/2}$, and observe that $\xi_H\propto\xi_0(1-t)^{-1/2}\gg\xi_0$ near T_c. (We use units in which $\hbar=c=k_B=1$.) Following Paper II, we assume $\Delta(\mathbf{r})=\Delta^B(\mathbf{r})+\Delta^{SL}(\mathbf{r})$, and require the *bulk* component $\Delta^B(\mathbf{r})$ to vary on the scale ξ_H. The *surface layer* component $\Delta^{SL}(\mathbf{r})$ should vanish for $z\gg\xi_0$. We can then separate the slowly varying part $(d/dz\sim\xi_H^{-1})$ and the rapidly varying part $(d/dz\sim\xi_0^{-1})$ on both sides of Eq. (4). In Paper II, we have shown that near T_c,

$$\int K(\mathbf{r},\mathbf{r}')\Delta^B(\mathbf{r}')d\mathbf{r}'=\mathbf{O}^B\Delta^B+\mathbf{O}^{SL}\Delta^B,$$

where $\mathbf{O}^B$ and $\mathbf{O}^{SL}$ are two differential operators, $\mathbf{O}^B\Delta^B$ being slowly varying and $\mathbf{O}^{SL}\Delta^B$ vanishing for $z\gg\xi_0$. Defining Δ^B to satisfy

$$\Delta^B=\mathbf{O}^B\Delta^B,\qquad(5)$$

then Δ^{SL} must satisfy a nonhomogeneous integral

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[14] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].

[15] By $V(z)$ we mean the phonon-mediated interaction between electrons which is responsible for the pair formation in superconductivity. It is usually assumed to be a constant throughout the sample and is denoted by V, g, or λ.

[16] To be exact, we should use the exact solution of $H_{c2}(T)$ for pure superconductors [E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966)] to calculate $\delta h(t)$. But, since it can be shown that Eq. (2) can also give exact result at $T=0$, the equation is likely to be a good approximation at all temperatures below T_c, so long as $L(T)<D$.

equation

$$\Delta^{SL}(\mathbf{r})+[1+V_1(z)/\lambda]\int K(\mathbf{r},\mathbf{r}')\Delta^{SL}(\mathbf{r}')d\mathbf{r}' =[V_1(z)/\lambda]\Delta^B(\mathbf{r})+[1+V_1(z)/\lambda]\mathbf{O}^{SL}\Delta^B(\mathbf{r}). \quad (6)$$

We have also shown in Paper II that in the gauge $A_x=H(z-z_0)$, $A_x=A_y=0$, $\Delta(\mathbf{r})$ can be limited to a real function of z only, and the most general boundary condition which Eq. (5) can take is

$$\xi_H(d/dz)\Delta(z)|_0=\alpha\Delta(0). \quad (7)$$

The parameter α can then be determined by requiring the source term (the right-hand side) in Eq. (6) to be orthogonal to the solution $\Delta(z)$ of the corresponding homogeneous integral equation.

Hence, we require

$$\int_0^\infty \Delta(z)\{\lambda^{-1}V_1(z)\Delta^B(z) +\lambda^{-1}[\lambda+V_1(z)]\mathbf{O}^{SL}\Delta^B(z)\}dz=0. \quad (8)$$

Equations (5)–(8) form a complete set of coupled equations which can be solved by an iteration method near T_c. In the GL region, Eq. (5) becomes simply the linearized GL equation and

$$\mathbf{O}^{SL}\Delta^B(z)=-2\chi_1(z)[d\Delta^B(z)/dz]_0,$$

where $\chi_1(z)$ is defined in II $[\chi_1(z)=0$ for $z\gg\xi_0]$. Also $\Delta^{SL}(z)\propto(\lambda_1/\lambda)\Delta^B(0)\ll\Delta^B(z)$. Thus to lowest order in λ_1/λ, Eq. (8) can be reduced to[17]

$$\alpha=1.426[N(0)|\lambda|]^{-1}(-\lambda_1/\lambda)(D/\xi_0)(\xi_H/\xi_0). \quad (9)$$

We shall also require $\alpha\ll1$ in region B, so that the boundary condition, Eq. (7), can be treated as a perturbation to the standard vanishing-slope boundary condition. In this case, $H\approx H_{c3}(\lambda)$ and $\xi_H\approx0.643\,\xi_0(1-t)^{-1/2}$, so that

$$\alpha\approx0.917[N(0)|\lambda|]^{-1}(-\lambda_1/\lambda)(D/\xi_0)\epsilon^{-1/2}.$$

Using the formulas given in Eqs. (II-40) and (II-41),[5] it follows that

$$\delta h=2.007[N(0)|\lambda|]^{-1}(-\lambda_1/\lambda)(D/\xi_0)\epsilon^{-1/2}. \quad (10)$$

Comparing (10) with (3), one finds

$$D_{\rm eff}=1.185D. \quad (11)$$

It can be shown that Eq. (11) corresponds to defining L by[18]

$$[\Delta(0)]^{-2}\int_0^\infty \Delta^2(z)dz\equiv C^{-1}\xi_H,$$

where H means $H_{c3}(\lambda)$ in this equation. The constant C was defined by Lüders independent of this identity, and its numerical value was found to be 0.762.[4]

From the requirement $\alpha\ll1$, we see that region B is bounded above by $(1-t)^{1/2}\gg Z'$ as well as bounded below by $(1-t)^{1/2}<\xi_0/D_{\rm eff}=Z/Z'$, while region A is characterized by $(1-t)^{1/2}>Z/Z'$.

Region C

This region is defined by $\alpha\gg1$ or $(1-t)^{1/2}\ll Z'$. In this region, the boundary condition can be treated as a perturbation to $\Delta^B(0)=0$. Clearly, $H_{c3}\to H_{c2}$ in this limit, so that $\xi_H\approx0.837\,\xi_0\epsilon^{-1/2}$, and $\alpha\approx1.194[N(0)|\lambda|]^{-1}\times(-\lambda_1/\lambda)(D/\xi_0)\epsilon^{-1/2}=0.595Z'\epsilon^{-1/2}$. Besides, in the present gauge, the physically most favored nucleation mode will correspond to a solution of the linearized GL equation with $\zeta_0\equiv z_0/\xi_H\gg1$, so that asymptotic expressions for the solution can be used to evaluate $\Delta^B(0)$ and $[d\Delta^B(z)/dz]_0$. When the boundary condition is matched by these values,

$$H_{c3}/H_{c2}\approx1+[(\zeta_0-\alpha)/(\zeta_0+\alpha)]2\pi^{-1/2}\zeta_0\exp[-\zeta_0^2].$$

We must still maximize the critical-field ratio with respect to ζ_0. Then we obtain[19]

$$\delta h\approx0.695[1-0.683Z'^{-1}\epsilon^{1/2}\exp(-0.354Z'^2\epsilon^{-1})]. \quad (12)$$

Interpolation formulas could be easily found between regions B and C, but we shall not do so here. We notice that regions A and/or B may not exist at all if $Z/Z'>1$ and/or $Z'\approx1$, respectively.

To summarize, we notice that the physics behind the problem is really very simple: Imagine both H_{c3} and H_{c2} plotted with respect to T near T_c, giving two nearly straight lines of somewhat different slopes. The two lines normally intersect the abscissa at the same point, i.e., at the transition temperature T_c, giving a constant ratio between them. But this need not always be the case, as the points of intersection are really the effective transition temperatures that enter in the formulas for $H_{c3}(T)$ and $H_{c2}(T)$, respectively, for the substitution of certain effective (or mean) interaction strengths that the superconducting regions see. Thus, by slightly suppressing the interaction strength near the surface

[17] Notice that Eqs. (7) and (9), when combined together and written into the form $(d/dz)\Delta(z)|_0=b^{-1}\Delta(0)$, are actually a boundary condition independent of the applied magnetic field. The above boundary condition is for the special gauge considered in this paper. For a general gauge, it should be changed to $(d/dz-2ieA_z)\times\Delta(z)|_0=b^{-1}\Delta(0)$, which is identical in form to the boundary condition proposed by de Gennes for the interface between a superconductor and a normal metal (both of thickness $\gg\xi_0$) in good contact. [See, for example, Ref. 13, p. 229 and Rev. Mod. Phys. **36**, 225 (1964).] Notice also that our boundary condition is for the *free surface* of a semi-infinite sample with slightly depressed interaction near the surface.

[18] This identity was first obtained by K.-D. Usadel (private communication); see also Ref. 4.

[19] R. O. Zaitsev, Zh. Eksperim. i Teor. Fiz. **50**, 1055 (1966) [English transl.: Soviet Phys.—JETP **23**, 702 (1966)] has arrived at a boundary condition very similar to our Eqs. (7) and (9) for a superconductor in contact with a normal metal. He thus can calculate H_{c3} in the GL region for such a sample, which looks very similar to our Eq. (12). But since his treatment applies to the $D\to\infty$ limit, while ours pertains to the case $D\sim\xi_0$ only, the predicted temperature dependences of the ratio H_{c3}/H_{c2} for the two cases are actually quite different from each other.

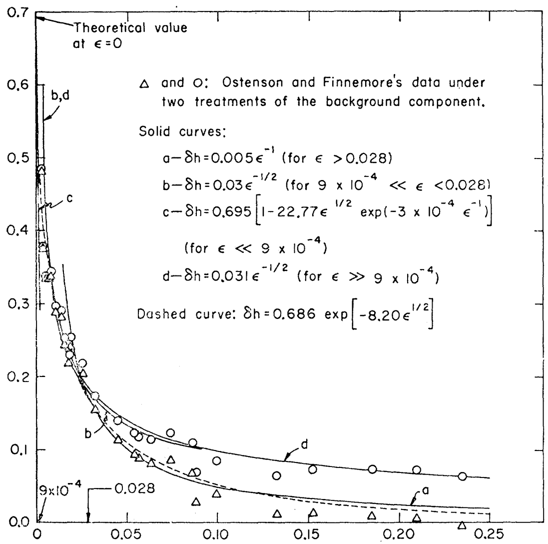

FIG. 1. Comparison of Ostenson and Finnemore's observation with the present theory. Open triangles are deviations of measured H_{c3}/H_{c2} from the emperically proposed background $1.695+0.285\epsilon$. Open circles are deviations of the same set of data from Eq. (1). Solid curves a, b, and c, are a theoretical fit of the open triangles by Eqs. (2), (3), and (12), using $Z\sim0.005$ and $Z'\sim0.03$, except that Eq. (2) has been replaced by its GL region equivalent. The solid curve d is a theoretical fit of the open circles by Eq. (3) using $Z'=0.031$. The dashed curve is the original empirical fit of the open triangles by $\alpha\exp(-\beta\epsilon^{1/2})$. The open circles are believed to correspond to a more correct treatment of the background component.

of a sample, one can produce a small parallel displacement of the H_{c3} line to the left of the H_{c2} line, if we temporarily assume that the superconducting surface sheath will always see the full perturbed interaction. The two lines can now intersect before reaching the abscissa. Thus, the ratio between them becomes drastically different from what it was before the displacement. Such a picture, however, is not exactly correct for T sufficiently close to T_c. First of all, by definition the value of $H_{c3}(T)$ should always be larger than that of $H_{c2}(T)$. Their ratio should therefore never drop below unity. Second, for T sufficiently close to T_c, the superconducting surface sheath will extend beyond the region of perturbed interaction strength, and the effects of the perturbation will be weakened by a factor equal to the ratio of the thickness of the perturbed region to that of the surface sheath. This causes the true H_{c3} curve to bend away from the shifted straight line and toward the unshifted straight line, as T approaches T_c. The above argument is based on the assumption that the nucleation processes are governed by the mean interaction strength in the superconducting region. It turns out that this assumption is not valid in a narrow temperature region still closer to T_c, because of the following third point. That is, when the width of the pair wave function becomes much larger than the dimension of a local perturbation, it becomes energetically more favorable for the pair wave function to respond to the perturbation locally, than to respond to the mean perturbed interaction. This ought to result in a further reduction of the effect of the local perturbation, and indeed our exact microscopic treatment of the problem in region C has led to this conclusion. Thus, the critical-field ratio will not drop to $-\infty$, as is predicted from the simple consideration using the argument given in the second point above. Instead, the ratio will merely drop to unity as T approached T_c, in accordance with our first point made above. The effect of the perturbation is seen to remain strong in the neighborhood of T_c even after using the exact microscopic treatment.

III. COMPARISON WITH EXPERIMENT AND FURTHER DISCUSSION

Let us now return to Ostenson and Finnemore's experiment. We notice that they obtained the background component of their H_{c3}/H_{c2} data by linearly extrapolating those data at $t\sim0.8$ toward $t\sim1$, with its slope slightly adjusted to reach Saint-James and de Gennes's value 1.695 at $T=T_c$. The deviation component δh is then the open triangles in Fig. 1. We could fit this set of data quite well by Eqs. (2), (3), and (12), with $Z\approx0.005$ and $Z'\approx0.03$.[20] This is given by curves a, b, and c in the figure. We, however, do not think that such a fit of the data is appropriate, since our present theory is valid only if Eq. (1) is valid for the background component. We therefore suggest finding δh by subtracting the data from Eq. (1) at various temperatures. This gives the open circles in Fig. 1. This time we find that formula (3) alone can fit the data quite well in the whole temperature region $0.003<\epsilon\lesssim0.25$ in which the precise data were taken, if one sets $Z'=0.031$ (curve d in Fig. 1). Since the temperature $T\approx0.75T_c$ still belongs to region B, it follows that $(Z/Z')^2\gtrsim0.25$, or equivalently, $D_{\text{eff}}\lesssim2\xi_0$. Formula (12) then merely guarantees that although Eq. (3) is used to interpret the data, it does not follow that the critical-field ratio will go to $-\infty$ as T approaches T_c, but will go to unity.

Now, since we have used a weak-coupling formula for $T_c(\lambda)$ on an almost strong coupling superconductor Nb, by $N(0)|\lambda|$ we should really mean the effective interaction introduced by Sheahen,[21] or in his notation, $N(0)V^*$. Using his value $N(0)V^*=0.77$ for single-crystal pure niobium, we find then $(-\delta V^*/V^*)(D/\xi_0)=1.19\%$ and $D<1.69\xi_0=726$ Å for the samples studied by Ostenson and Finnemore. If we could see the onset of region A at some lower temperature, we could even determine $-\delta V^*/V^*$ and D/ξ_0 separately, but not with the present data supplied in Ref. 6.

[20] We have not actually used the exact form of Eq. (2) for the curve fitting, but have replaced it by its GL region equivalent, $\delta h=Z\epsilon^{-1}$, since any nondivergent component of δh should have been removed by Ostenson and Finnemore's treatment of the background component.

[21] T. P. Sheahen, Phys. Rev. **149**, 370 (1966).

Therefore, the present theory can account for Ostenson and Finnemore's phenomenon rather well. We wish to emphasize the following two points: (1) This interpretation of the phenomenon is by no means unique, nor is it necessarily correct, even if critical fluctuations can be ruled out of consideration. The reason is that if any physical quantity, which enters in the mean-field–theory formula for T_c, is perturbed near the surface for a distance of the order of the zero-temperature coherence length, then the above discussion applies with little change, and essentially identical conclusions are expected to follow. Thus, in principle, a surface perturbation to any of the following quantities is expected to produce the same effects as Ostenseon and Finnemore observed: (a) the interaction parameter λ (as discussed above), (b) the Debye cutoff frequency ω_D, (c) the electron density of states at the Fermi surface $N(0)$, (d) the magnetic-impurity concentration, (e) the nonmagnetic-impurity concentration *if* the sample is either a two-band superconductor[22] or an anisotropic one,[23] etc. Particular attention is called to the last item because niobium is both a two-band superconductor and anisotropic, while an impurity nonhomogeneity near the surface is very likely to exist in the samples studied by Ostenson and Finnemore as they remarked.[6] Notice that if the local-impurity concentration can indirectly affect the transition temperature, through changing one or more of the items (a), (b), and (c) listed above, then the nonmagnetic-impurity concentration must also be included in the list even for a simple BCS superconductor. This is presumably what is called the valence effect.[23] (2) Even if the present theory is not the correct explanation of Ostenson and Finnemore's experiment, we believe that it is still at least an observable phenomenon. For example, one can prepare a sample by coating a bulk superconductor with a layer of another superconductor having a slightly different value for any one of the above-listed quantities. But it is necessary that the coating layer be of a thickness of the order of the zero-temperature coherence length (assumed roughly the same for both layers) and that the contact between the layers be so good that scattering of electrons at the interface be essentially negligible. (The coating layer should preferably be an isotope of the bulk material.) In this case, another interesting situation with $(\lambda_1/\lambda)>0$ can also be investigated. We expect that the critical-field ratio will rise above the value given by the simple picture near T_c, but that the division of the temperature range between absolute zero and T_c into three non-overlapping subregions A, B, and C is still appropriate. In regions A and B, we expect that the discussions given in this paper, in particular the formulas given in Eqs. (2) and (3), are still valid. The reader should keep in mind that Z and Z' are negative in this case, and should be replaced by their absolute values in determining the boundaries of these regions. In region C, our conclusions are no longer valid for this case, and the exact behavior of the critical-field ratio H_{c3}/H_{c2} in the immediate neighborhood of T_c is still unknown.

Note added in proof. Since this paper was submitted for publication, the author has received several preprints on the experimental aspects of this subject. J. E. Ostenson, J. R. Hopkins, and D. K. Finnemore reported more systematic investigations of the phenomenon which two of them (JEO and DKF) discovered earlier. F. de la Cruz, M. D. Moloney, and M. Cardona of Brown University confirmed the observation of Ostenson and Finnemore by studying tin-rich Sn-In alloys, but observed a sharp rise of the critical-field ratio H_{c3}/H_{c2} above the Saint James-de Gennes value of 1.695 near T_c for indium-rich In-Bi alloys. This latter phenomenon was also observed independently by R. W. Rollins, R. L. Capelletti, and J. H. Fearday of Ohio University by studying lead rich Pb-In alloys. While the observed sharp rise of the ratio H_{c3}/H_{c2} may not yet be directly associated with the case of $\lambda_1/\lambda>0$ discussed near the end of this paper, it appears that the diversity of the experimental results lends some support to the hypothesis that slight sample inhomogeneities, rather than critical fluctuations, are the cause of the observed phenomena.

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[22] V. A. Moskalenko and M. E. Palistant, Zh. Eksperim. i Teor. Fiz. **49**, 770 (1965) [English transl.: Soviet Phys.—JETP **22**, 536 (1966)].

[23] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).