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Thermodynamics of Volume and Pressure Effects for Type-II Superconductors*

R. R. Hake
North American Aviation Science Center, Thousand Oaks, California

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Some thermodynamic relationships which include volume and pressure effects are presented for the case of the ideal bulk type-II superconductor. On the basis of published data, it is assumed that the upper-critical-field transition at (H_{c2}, T_s) occurs without discontinuities in the entropy and magnetization and without infinite discontinuities in the second-order derivatives of the Gibbs free energy. For an ellipsoidal specimen in an applied field **H** directed along a principal axis at (H_{c2}, T_s), Clapeyron- and Ehrenfest-type equations yield $\Delta V=0$, $\Delta K=(S_o/4\pi V)(\partial H_{c2}/\partial P)^2{}_T$, and $\Delta\beta=(-S_o/4\pi V)(\partial H_{c2}/\partial P)_T(\partial H_{c2}/\partial T)_P$. Here Δ indicates the difference between the superconducting- and normal-state values at constant H; V is the specimen volume (which is shown to be field-dependent in the superconducting type-II mixed state); $K=-V^{-1}(\partial V/\partial P)_{H,T}$ is the isothermal compressibility; $\beta\equiv V^{-1}(\partial V/\partial T)_{H,P}$ is the thermal expansivity; and $S_o\equiv\{\partial[4\pi(I_s-I_n)]/\partial H\}_{P,T}$, where I_s and I_n are the total superconducting- and normal-state magnetic moments and the derivative is taken at (H_{c2}, T_s).

I. INTRODUCTION

ALTHOUGH the standard thermodynamic analysis originally developed by Keesom, Rutgers, Gorter, and Casimir for the ideal bulk type-I superconductor is well known,[1,2] there appears to be no comparable treatment for the case of the ideal bulk type-II superconductor. In the present paper[3] we outline such a treatment which includes volume and pressure effects. Since relatively little is known about the ideal reversible type-II lower-critical-field transition at H_{c1},[4] we focus attention here on type-II properties in zero magnetic field and at the upper critical field H_{c2}.

II. STANDARD FORMULAS

As usual,[1,2] we define a "magnetic Gibbs free energy" G [everywhere continuous across the transition surface in H (*applied* magnetic field), T, P space] such that

$$dG=-SdT-IdH+VdP, \tag{1}$$

where S is the total entropy of the specimen, I is the total magnetic moment of the specimen, and V is the specimen volume. For simplicity, we shall assume that **H** is directed along a principal axis of an ellipsoidal specimen so that the magnetization **m** per unit volume is uniform and also directed along the principal axis. Thus **H** is parallel to the total magnetic moment $\mathbf{I}=\mathbf{m}V$ and vector notation is not required.

From Eq. (1), the first derivatives of G are

$$S=-(\partial G/\partial T)_{H,P}, \tag{2a}$$

$$I=-(\partial G/\partial H)_{T,P}, \tag{2b}$$

$$V=(\partial G/\partial P)_{H,T}, \tag{2c}$$

and the second derivatives of G are

$$C/T=(\partial S/\partial T)_{H,P}=-(\partial^2 G/\partial T^2)_{H,P}, \tag{3a}$$

$$KV=-(\partial V/\partial P)_{H,T}=-(\partial^2 G/\partial P^2)_{H,T}, \tag{3b}$$

$$\beta V=(\partial V/\partial T)_{H,P}=(\partial^2 G/\partial T\partial P)_H, \tag{3c}$$

where C is the total heat capacity of the specimen, K is the isothermal compressibility, and β is the thermal expansivity, all at constant applied field H.

From Eq. (1) and the condition that the order in which partial derivatives of G are taken is immaterial, the Maxwell relationships follow:

$$(\partial V/\partial H)_{T,P}=-(\partial I/\partial P)_{T,H}, \tag{4a}$$

$$(\partial V/\partial T)_{P,H}=-(\partial S/\partial P)_{T,H}, \tag{4b}$$

$$(\partial I/\partial T)_{P,H}=(\partial S/\partial H)_{T,P}. \tag{4c}$$

III. DIFFERENCES BETWEEN SUPERCONDUCTING STATE AND NORMAL STATE IN ZERO FIELD

For the type-II superconductor we can arbitrarily *define* a "thermodynamic" critical field H_c such that, independent of specimen shape,

$$[G_n(0)-G_s(0)]_{T,P}\equiv V_s(0)H_c^2/8\pi, \tag{5}$$

where (0) indicates the value at $H=0$, and subscripts n and s, respectively, designate normal and supercon-

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[1] A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, London, 1961), pp. 129–135.

[2] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1952), pp. 56–77.

[3] A preliminary version of this work has been reported by R. R. Hake, in *Proceedings of the Conference on the Physics of Type-II Superconductivity*, edited by B. S. Chandrasekhar (Western Reserve University, Cleveland, Ohio, 1964), Vol. I, pp. I–15.

[4] For a review see B. Serin, in A Treatise on Superconductivity, edited by R. D. Parks (unpublished).

ducting states. We shall use subscript s and the term "superconducting state" to indicate any thermodynamically reversible superconductinglike condensed phase, e.g., the Abrikosov[5] "mixed" or vortex phase, or the nearly perfectly diamagnetic Meissner phase existing below the lower critical field H_{c1} in zero-demagnetizing-coefficient ("zero n") type-II superconductors and below the thermodynamic critical field H_c in zero-n type-I superconductors. We shall not make the usual approximation that G_n (hence I_n, S_n, V_n, C_n, K_n, β_n) is independent of H, since for extreme type-II superconductors with very high upper critical fields, i.e., H_{c2} $(T=0)\gtrsim 50$ kG, recent magnetization measurements[6–8] indicate that $(\partial I_n/\partial H)_{P,T}$ is comparable with $(\partial I_s/\partial H)_{P,T}$ at high $H\leq H_{c2}$.

For a type-II superconductor, H_c can be obtained from the area between the *reversible* superconducting- and normal-state magnetization curves, since, from Eqs. (1) and (5) and the condition $G_n(H_{c2}, T_s)=G_s(H_{c2}, T_s)$,

$$\frac{V_s(0)H_c^2}{8\pi}=\int_0^{H_{c2}}(I_n-I_s)dH, \tag{6}$$

where the integration is at constant (T, P). Alternatively, from Eq. (3a), $G_n(0)$ and $G_s(0)$ and hence H_c can be obtained[9–12] via a double integration of (H, T)-history-independent specific-heat data. If γ (the electronic specific-heat coefficient per unit volume) and T_c (the zero-field superconducting transition temperature) are known, then H_c can be estimated from the BCS expression[13]

$$H_c\approx H_0[1-(T/T_c)^2]\approx 2.42\gamma^{1/2}T_c[1-(T/T_c)^2]. \tag{7}$$

Differentiating Eq. (5) at $H=0$ in accordance with Eqs. (2) and (3) yields specimen-shape-independent differences in first- and second-order derivatives of G between the type-II zero-field superconducting state and the zero-field normal state:

$$[S_n(0)-S_s(0)]_{T,P}=-\frac{VH_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_P-\left\{\frac{H_c^2}{8\pi}\left(\frac{\partial V}{\partial T}\right)_P\right\}, \tag{8a}$$

$$[S_n(0)-S_s(0)]_{T_c,P}=0, \tag{8b}$$

$$[C_s(0)-C_n(0)]_{T,P}=\frac{VT}{4\pi}\left[H_c\left(\frac{\partial^2 H_c}{\partial T^2}\right)_P+\left(\frac{\partial H_c}{\partial T}\right)_P^2\right]+\left\{\frac{H_cT}{4\pi}\left[\frac{H_c}{2}\left(\frac{\partial^2 V}{\partial T^2}\right)_P+2\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial H_c}{\partial T}\right)_P\right]\right\}, \tag{9a}$$

$$[C_s(0)-C_n(0)]_{T_c,P}=(VT_c/4\pi)(\partial H_c/\partial T)^2_P, \tag{9b}$$

$$[V_s(0)-V_n(0)]_{T,P}=-\frac{VH_c}{4\pi}\left(\frac{\partial H_c}{\partial P}\right)_T-\left\{\frac{H_c^2}{8\pi}\left(\frac{\partial V}{\partial P}\right)_T\right\}, \tag{10a}$$

$$[V_s(0)-V_n(0)]_{T_c,P}=0, \tag{10b}$$

$$[K_s(0)-K_n(0)]_{T,P}=\frac{1}{4\pi}\left[H_c\left(\frac{\partial^2 H_c}{\partial P^2}\right)_T+\left(\frac{\partial H_c}{\partial P}\right)_T^2\right]+\left\{\frac{H_c}{4\pi V}\left[\frac{H_c}{2}\left(\frac{\partial^2 V}{\partial P^2}\right)_T+2\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial H_c}{\partial P}\right)_T\right]\right\}, \tag{11a}$$

$$[K_s(0)-K_n(0)]_{T_c,P}=(1/4\pi)(\partial H_c/\partial P)^2_T, \tag{11b}$$

$$[\beta_s(0)-\beta_n(0)]_{T,P}=-\frac{1}{4\pi}\left[H_c\left(\frac{\partial^2 H_c}{\partial T\partial P}\right)+\left(\frac{\partial H_c}{\partial P}\right)_T\left(\frac{\partial H_c}{\partial T}\right)_P\right]-\left\{\frac{H_c}{4\pi V}\left[\frac{H_c}{2}\left(\frac{\partial^2 V}{\partial T\partial P}\right)+\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial H_c}{\partial T}\right)_P+\left(\frac{\partial H_c}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right]\right\}, \tag{12a}$$

$$[\beta_s(0)-\beta_n(0)]_{T_c,P}=-(1/4\pi)[(\partial H_c/\partial P)_T(\partial H_c/\partial T)_P]. \tag{12b}$$

In most cases, we expect the terms in { } brackets to be relatively small.[14] For notational simplicity we have set $V_s(0)=V$. Equations (8b), (9b), (10b), (11b), (12b) are also valid for a type-I superconductor,[1,2] independent of specimen shape. Equations (8a), (9a), (10a), (11a), (12a) are valid for a type-I superconductor, independent of its shape, if H_c is defined as in Eq. (5). [Except for usually negligibly small magnetostrictive,[14] penetration depth, and normal-state magnetization corrections, H_c as defined by Eq. (5) is identical to the critical field H_c for the destruction of superconductivity in a magnetically reversible,

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[6] R. R. Hake, Phys. Rev. Letters **15**, 865 (1965).
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[12] L. J. Barnes and R. R. Hake, Phys. Rev. **153**, 435 (1967); Ann. Acad. Sci. Fennicae, Ser A VI, **210**, 78 (1966).
[13] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[14] For a discussion of the relative magnitudes involved in typical cases, see Ref. 2, pp. 73–77. For a more recent compilation of experimental values of $(\partial H_c/\partial P)_T$ showing its wide variability for different elements (even changing sign), see M. Levy and J. L, Olsen, in *Physics of High Pressure and the Condensed Phase*, edited by A. Van Itterbeek (North-Holland Publishing Co. Amsterdam, 1965), p. 525.

zero-n type-I specimen.] Alternatively, equations similar to Eqs. (8a), (9a), (10a), (11a), (12a) with (0) replaced by (H_c) can be obtained[1] for zero-n type-I superconductors from the Clapeyron equations valid at the transition surface in (H, P, T) space.

IV. DIFFERENCES BETWEEN SUPERCONDUCTING STATE AND NORMAL STATE AT THE UPPER CRITICAL FIELD

A. Clapeyron Equations

The Gibbs free energy G is everywhere continuous across the H_{c2} transition surface in (H, P, T) space between the mixed state and the normal state (we ignore the "sheath state"[15] here, assuming that it has negligible effect on the *reversible bulk* thermodynamic parameters). Thus differential displacements of G taken parallel to the transition surface just inside (dG_s) and just outside (dG_n) must be equal. Considering displacements at constant P, H, and T, we obtain, respectively, the Clapeyron equations:

$$(\partial H_{c2}/\partial T)_P = [S_n(H_{c2})-S_s(H_{c2})]/[I_s(H_{c2})-I_n(H_{c2})], \quad (13)$$

$$(\partial T_s/\partial P)_H = [V_n(H_{c2})-V_s(H_{c2})]/[S_n(H_{c2})-S_s(H_{c2})], \quad (14)$$

$$(\partial H_{c2}/\partial P)_T = [V_s(H_{c2})-V_n(H_{c2})]/[I_s(H_{c2})-I_n(H_{c2})]. \quad (15)$$

Thus far, magnetization measurements[4,6–8,16] on type-II specimens, covering a wide Gor'kov-Goodman-calculated[16] Ginzburg-Landau κ_G range, $0.71\leq\kappa_G\leq 100$, indicate

$$I_s(H_{c2})-I_n(H_{c2})=0, \quad (16)$$

and calorimetric measurements[4,9–12,16–19] in the presence of magnetic fields on type-II specimens with $0.85\leq\kappa_G\leq 68$ suggest

$$S_n(H_{c2})-S_s(H_{c2})=0. \quad (17)$$

Assuming the general validity[20] of Eqs. (16) and (17), Eq. (13) becomes indeterminate [experimentally, $(\partial H_{c2}/\partial T)_P$ appears to be nowhere infinite, so that Eqs. (13) and (16) imply Eq. (17)]. Since an infinite $(\partial T_s/\partial P)_H$ is unreasonable, Eqs. (14) and (17) imply

$$V_n(H_{c2})-V_s(H_{c2})=0, \quad (18)$$

and Eqs. (14) and (15) also become indeterminate. Equation (18) has apparently not been checked experimentally.[21]

B. Ehrenfest Equations

From the direct and indirect experimental evidence supporting Eqs. (16)–(18), we shall assume that the first-order derivatives of G (viz., S, I, V) are everywhere continuous across the H_{c2} transition surface in (H, P, T) space. Calorimetric measurements[4,9–12,16–19] on type-II superconductors suggest that along H_{c2} the ideal zero-transition-breadth type-II superconductor would be characterized by *finite* discontinuities in the specific heat and, by inference, other second-order derivatives of the Gibbs function, in contrast to the *infinite* discontinuities which appear to characterize the λ transition in liquid helium[22] and possibly the type-II lower-critical-field transition at H_{c1}.[4] The idealized type-II upper-critical-field transition then appears to be a rare (possibly unique) example of a transition which is second order in the sense described by Ehrenfest[23] *at all points* on the transition surface. Thus we utilize the Ehrenfest approach and write, e.g., considering displacement of S along and on either side of the transition surface at constant P,

$$(\partial S_n/\partial H)_{P,T}dH+(\partial S_n/\partial T)_{P,H}dT=(\partial S_s/\partial H)_{P,T}dH+(\partial S_s/\partial T)_{P,H}dT. \quad (19)$$

From relationships such as Eq. (19), considering in order displacements of S, I, V at constant P [Eq. (20)], at constant H [Eq. (21)], and at constant T [Eq. (22)], we obtain

$$\left(\frac{\partial H_{c2}}{\partial T}\right)_P = \frac{(\partial S_s/\partial T)_{P,H}-(\partial S_n/\partial T)_{P,H}}{(\partial S_n/\partial H)_{P,T}-(\partial S_s/\partial H)_{P,T}} \quad (20a)$$

$$= \frac{(\partial I_s/\partial T)_{P,H}-(\partial I_n/\partial T)_{P,H}}{(\partial I_n/\partial H)_{P,T}-(\partial I_s/\partial H)_{P,T}} \quad (20b)$$

$$= \frac{(\partial V_s/\partial T)_{P,H}-(\partial V_n/\partial T)_{P,H}}{(\partial V_n/\partial H)_{P,T}-(\partial V_s/\partial H)_{P,T}}, \quad (20c)$$

$$\left(\frac{\partial P}{\partial T}\right)_H = \frac{(\partial S_s/\partial T)_{H,P}-(\partial S_n/\partial T)_{H,P}}{(\partial S_n/\partial P)_{H,T}-(\partial S_s/\partial P)_{H,T}} \quad (21a)$$

$$= \frac{(\partial I_s/\partial T)_{H,P}-(\partial I_n/\partial T)_{H,P}}{(\partial I_n/\partial P)_{H,T}-(\partial I_s/\partial P)_{H,T}} \quad (21b)$$

$$= \frac{(\partial V_s/\partial T)_{H,P}-(\partial V_n/\partial T)_{H,P}}{(\partial V_n/\partial P)_{H,T}-(\partial V_s/\partial P)_{H,T}}, \quad (21c)$$

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[16] For a review of early low-κ_G magnetization and specific-heat measurements, and the Gor'kov-Goodman formula, see E. A. Lynton, *Superconductivity* (Methuen and Company, Ltd., London, 1964), 2nd ed., pp. 67 ff.

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[21] Preliminary length measurements on the type-II superconductor Nb by E. Fawcett and G. K. White appear to be in qualitative accord with Eq. (18) and suggest a field-dependent length in the mixed state as indicated in the present analysis. G. K. White (private communication).

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[23] P. Ehrenfest, Commun. Phys. Lab. Univ. Leiden, Suppl. No. 75b, 1933 (unpublished).

$$\left(\frac{\partial H_{c2}}{\partial P}\right)_T = \frac{(\partial S_s/\partial P)_{T,H} - (\partial S_n/\partial P)_{T,H}}{(\partial S_n/\partial H)_{T,P} - (\partial S_s/\partial H)_{T,P}} \quad (22a)$$

$$= \frac{(\partial I_s/\partial P)_{T,H} - (\partial I_n/\partial P)_{T,H}}{(\partial I_n/\partial H)_{T,P} - (\partial I_s/\partial H)_{T,P}} \quad (22b)$$

$$= \frac{(\partial V_s/\partial P)_{T,H} - (\partial V_n/\partial P)_{T,H}}{(\partial V_n/\partial H)_{T,P} - (\partial V_s/\partial H)_{T,P}}. \quad (22c)$$

By straightforward manipulation of Eqs. (20)–(22) [after substitutions indicated by Eqs. (3) and (4)], some useful Ehrenfest relationships, Eqs. (23)–(27) can be derived[24] for type-II superconductors. Subject to the validity of Eqs. (16)–(18) and the condition that second-order derivatives of G do not become infinite at the upper-critical-field transition, Eqs. (23)–(27) should be valid for any ellipsoidal type-II specimen in an applied field H directed along a principal axis:

$$[C_s(H_{c2}) - C_n(H_{c2})] = T_s(\partial H_{c2}/\partial T)^2{}_P[(\partial I_s/\partial H)_{P,T_s} - (\partial I_n/\partial H)_{P,T_s}], \quad (23)$$

$$[K_s(H_{c2}) - K_n(H_{c2})] = V^{-1}(\partial H_{c2}/\partial P)^2{}_T[(\partial I_s/\partial H)_{P,T_s} - (\partial I_n/\partial H)_{P,T_s}], \quad (24)$$

$$[\beta_s(H_{c2}) - \beta_n(H_{c2})] = -V^{-1}(\partial H_{c2}/\partial P)_T(\partial H_{c2}/\partial T)_P[(\partial I_s/\partial H)_{P,T_s} - (\partial I_n/\partial H)_{P,T_s}], \quad (25)$$

$$(\partial T_s/\partial P)_H = [K_s(H_{c2}) - K_n(H_{c2})]/[\beta_s(H_{c2}) - \beta_n(H_{c2})] \quad (26)$$

$$= VT_s[\beta_s(H_{c2}) - \beta_n(H_{c2})]/[C_s(H_{c2}) - C_n(H_{c2})], \quad (27)$$

where pressure derivatives of T_s and H_{c2} are related by

$$(\partial T_s/\partial P)_H = -(\partial H_{c2}/\partial P)_T/(\partial H_{c2}/\partial T)_P, \quad (28)$$

$(\partial I_s/\partial H)_{P,T_s}$ means that the derivative is taken at constant (P, T) at the transition surface where $T = T_s$ and $H = H_{c2}$, and for notational simplicity we have set $V_n(H_{c2}) = V_s(H_{c2}) = V$. Equation (23) was apparently first derived by Goodman.[25]

Evidently only Eq. (23) has been checked via direct substitution of experimental data.[11,12,17] Discontinuities in the bulk modulus $B \equiv K^{-1}$ at H_{c2} have been deduced from elastic-moduli data on type-II Pb-Tl alloys by Alers and Karbon.[26] As far as we are aware, no measurements of discontinuities in thermal expansivity β at H_{c2} or measurements of $(\partial T_s/\partial P)_H$ at H_{c2} have been reported, although there have been measurements of zero-field values of $\Delta\beta$ for the type-II Nb_3Sn [27] and zero-field values of $\partial T_s/\partial P$ for the type-II superconductors Nb_3Sn,[28–30] V_3Ga,[29] V_3Si,[29] Nb–25 at.% Zr,[30] La,[31] V,[32] and Nb.[32]

V. COMPARISON OF THE TYPE-II SUPERCONDUCTING STATE AT ZERO FIELD AND AT THE UPPER CRITICAL FIELD

Comparison of Eq. (8a) with (17) and Eq. (10a) with (18) shows that $S_{P,T}$ and $V_{P,T}$ for a type-II superconductor must be field-dependent below H_{c2} since, in most cases, one expects[33] that even for extreme type-II superconductors[6–8] $|[S_n(H_{c2}) - S_n(0)]| \equiv |\Delta S_n(H_{c2})| < |\Delta S_s(H_{c2})|$, and likewise $|\Delta V_n(H_{c2})| <$

[24] To obtain Eq. (23), apply Eqs. (3a) and (4c) to Eq. (20a), then multiply by Eq. (20b). To obtain Eq. (24), apply Eq. (4a) to Eq. (22b) and apply Eq. (3b) to Eq. (22c), then multiply the resulting equations together. To obtain Eq. (25), apply Eqs. (3c) (4b), and (4c) to Eq. (22a), then multiply by Eq. (20b). To obtain Eq. (26), divide Eq. (24) by Eq. (25). To obtain Eq. (27), divide Eq. (25) by Eq. (23).

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[31] T. F. Smith and W. E. Gardner, Phys. Rev. **146**, 291 (1966).

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[33] From Eqs. (2a) and (2b), $S_n(H_{c2}) - S_n(0) \equiv \Delta S_n(H_{c2}) = (H_{c2}^2/2)[V_n(\partial\chi_n/\partial T)_{P,Hc2} + \chi_n(\partial V_n/\partial T)_{P,Hc2}]$, neglecting magnetostriction and assuming that the normal-state susceptibility χ_n per unit volume is independent of H. Order-of-magnitude estimates suggest that for typical extreme type-II superconductors which do not contain localized magnetic moments, both terms in the [ ] brackets should be extremely small, leading to

$$|\Delta S_s(H_{c2})| > |\Delta S_n(H_{c2})|.$$

Likewise, from Eqs. (2b) and (2c),

$$\Delta V_n(H_{c2}) = -(H_{c2}^2/2)[V_n(\partial\chi_n/\partial P)_{Hc2,Ts} + \chi_n(\partial V/\partial P)_{Hc2,Ts}],$$

and order-of-magnitude estimates suggest

$$|\Delta V_s(H_{c2})| > |\Delta V_n(H_{c2})|.$$

$|\Delta V_s(H_{c2})|$. This H dependence of $S_{P,T}$ [34] and $V_{P,T}$ [21] in the field-penetrated mixed state at $H_{c1} \leq H < H_{c2}$ contrasts with the type-I case where the field is almost totally excluded from the bulk of a zero-n specimen below H_c, so that $S_{P,T}$ and $V_{P,T}$ (except for magnetostriction) are field-independent for $0 \leq H < H_c$. The field dependence of S over a wide field region in the *mixed state* of type-II superconductors[34] opens up some interesting possibilities for cooling via their adiabatic magnetization[35] without type-I *intermediate-state* eddy-current losses.

It is of interest to compare the Rutgers equation (9b) for $[C_s(0) - C_n(0)]_{T_c,P} \equiv \Delta C_R(T_c)$ with the Ehrenfest equation (23) for $[C_s(H_{c2}) - C_n(H_{c2})] \equiv \Delta C_E(T_s)$, where $T_s < T_c$, since in Eq. (23) $(\partial I_s/\partial H)_{P,T_s}$ is not defined at $T_s = T_c$, $H_{c2} = 0$.[36,37] If we substitute into Eq. (23) an expression for $(\partial H_{c2}/\partial T)^2{}_P$ in terms of $(\partial H_c/\partial T)_P$ obtained by differentiating the Abrikosov[5] expression as generalized by Maki,[38]

$$H_{c2}(T) = \sqrt{2}\kappa_1(T) H_c(T), \quad (29)$$

and if we further substitute into Eq. (23) the zero-n Abrikosov-Maki expression for the limiting slope of the magnetization versus applied field curve at the upper critical field H_{c2} (as generalized to properly include the very high-κ_G case[6–8]),

$$(\partial I_s/\partial H)_{P,T_s} - (\partial I_n/\partial H)_{P,T_s} \equiv S_o/4\pi$$
$$= V[4\pi(2\kappa_2^2 - 1)\beta_0]^{-1}, \quad (30)$$

where $\beta_0 = 1.16$ for a triangular vortex lattice,[4] then in the limit as $T_s \to T_c$ and $\kappa_2 \to \kappa_1(T_c) \equiv \kappa_0$,[38] the ratio of the Ehrenfest and Rutgers expressions for ΔC becomes for the zero-n case

$$A \equiv [\lim_{T_s \to T_c} \Delta C_E(T_s)]/\Delta C_R(T_c) = 2\kappa_0^2[(2\kappa_0^2 - 1)1.16]^{-1}, \quad (31)$$

so that $A(\kappa_0 = 1.9) = 1$, $A(\kappa_0 \to 1/\sqrt{2}) \to \infty$, and $A(\kappa_0 \to \infty) \to 0.86$. It has been suggested[39] that in the limit as $T_s \to T_c$, the specific-heat jump ΔC_1 associated with the lower-critical-field transition at H_{c1} should add to ΔC_E, so that

$$\lim_{T_s \to T_c} [\Delta C_E(T_s) + \Delta C_1(T_s)]/\Delta C_R(T_c) = 1, \quad (32)$$

for all κ such that Eq. (30) is preserved. Equation (32) might be a useful result, since it would appear to determine $\lim_{T_s \to T_c} \Delta C_1$ as a function of κ_0, assuming the validity of Eqs. (9b), (23), (29), and (30) as $T_s \to T_c$. However, strictly speaking, for finite-size specimens $\lim_{T_s \to T_c} \Delta C_1 = 0$, because, in analogy with the parallel-field, thin-film case, the lower-critical-field transition at H_{c1} should be suppressed[40] as $T_s \to T_c$ and the penetration depth $\lambda \to \infty$, although $H_{c2}(T_s \to T_c)$ retains its significance as a second-order transition field between superconducting and normal phases. If then we formally require

$$\lim_{T_s \to T_c} \Delta C_E(T_s)/\Delta C_R(T_c) = 1, \quad (33)$$

and assume Eqs. (9b), (23), and (29) to be correct, then we obtain

$$\lim_{T_s \to T_c} (S_o/4\pi) = V(4\pi 2\kappa_0^2)^{-1}. \quad (34)$$

Because of the numerous experimental difficulties in obtaining meaningful specific-heat and magnetization data very close to T_c, Eqs. (33) and (34) are probably only of academic interest for bulk materials,[41] although they may be of some significance for the parallel-field very-thin-film case.[42]

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[34] In Refs. 10 and 11, $S(H, T)$ in the type-II mixed state, derived by direct integration of (H, T)-history-independent specific-heat data taken in the presence of magnetic fields $0 \leq H \leq H_{c2}$, is shown graphically for V–5 at.% Ta ($\kappa_G \approx 5$) (Ref. 10) and V ($\kappa_G \approx 0.98$) (Ref. 11).

[35] Nearly *reversible* magnetocaloric cooling and heating in the type-II mixed state have independently been observed in well-annealed specimens by R. R. Hake and L. J. Barnes, in *Proceedings of the Ninth International Conference on Low-Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, New York, 1965), p. 513; and T. Ohtsuka, Phys. Letters **17**, 196 (1965). More recent work has been reported by R. B. Flippen, J. Appl. Phys. **37**, 1010 (1966); S. M. Wasmin, G. G. Grenier, and N. H. Zebouni (to be published); T. Ohtsuka and N. Takano (to be published).

[36] T. G. Berlincourt, G. D. Cody, and C. J. Gorter have all independently noted the apparent mismatch of Eqs. (9b), (23), (29), and (30) near T_c (private communications). C. J. Gorter has pointed out a connection between the Ehrenfest and Rutgers expressions for ΔC near T_c [Rev. Mod. Phys. **36**, 27 (1964)].

[37] Similar arguments leading to Eq. (34) also follow from comparison of Eq. (11b) with Eq. (24) or comparison of Eq. (12b) with Eq. (25).

[38] K. Maki, Physics **1**, 21 (1964).

[39] P. M. Marcus, in *Proceedings of the Conference on the Physics of Type-II Superconductivity*, edited by B. S. Chandrasekhar (Western Reserve University, Cleveland, Ohio, 1964), Vol. III, p. 1. B. B. Goodman, *ibid.*, p. 56.

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[41] Following Ref. 11, one can experimentally define $A_{\mathrm{exp}} \equiv \lim_{T_s \to T_c} [C_s(H_{c2}) - C_n(H_{c2})]_{P,H}/[C_s(0) - C_n(0)]$, where the "limit" is obtained by extrapolation of data taken for $T_s < T_c$. Extrapolation of data for $T_s \lesssim 0.98 T_c$ yields A_{exp} values in reasonable agreement with the right-hand side of Eq. (31) with κ_0 set equal to κ_G for V ($\kappa_G \approx 0.98$) (Ref. 11), V–5 at.% Ta ($\kappa_G \approx 5$), (Ref. 9), and T–16 at.% Mo ($\kappa_G \approx 68$) (Ref. 12). Thus Eqs. (9b), (23), (29), and (30) appear to be obeyed in bulk materials at $T_s/T_c \lesssim 0.98$.

[42] E. Guyon, F. Meunier, and R. S. Thompson, Phys. Rev. **156**, 452 (1967). Their Eq. (3.18), attributed to A. Baratoff and R. S. Thompson, appears to be consistent with Eq. (34).