mined in this study. It was observed, however, that He^3 at 15.98°K and 1341 atm still has the hexagonal close-packed structure. The cell dimensions and molar volume at this condition are: $c_0=4.986$ A, $a_0=0.046$ A, $c_0/a_0=1.637$, and $V=12.07$ cc. The computed[4] molar volume is 12.09 cc.

The new phase has been designated the γ phase.

We wish to acknowledge the many contributions of Donald F. Clinton and the members of his staff shop in the construction and repair of items of equipment used in this research.

---

†Work performed under the auspices of the U. S. Atomic Energy Commission.

[1]J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) A218, 291 (1953).

[2]R. L. Mills and A. F. Schuch, Phys. Rev. Letters 6, 263 (1961).

[3]F. J. Edeskuty, Ind. Eng. Chem. 51, 69(A) (1959).

[4]E. R. Grilly and R. L. Mills, Ann. Phys. 8, 1 (1959).

SIMPLE MODEL FOR THE MAGNETIC BEHAVIOR OF SUPERCONDUCTORS OF NEGATIVE SURFACE ENERGY

B. B. Goodman
Institut Fourier, Grenoble, France
(Received April 12, 1961)

It is well known that for certain superconductors the magnetic field H_c^* required for the complete suppression of the superconducting state considerably exceeds the critical field H_c. Interest in this question has been revived by the discovery that, well below their transition temperatures, exceptionally high values of H_c^* are found for Mo_3Re[1] (≈ 15 kgauss) and Nb_3Sn[2] (>88 kgauss). While inhomogeneous strains and chemical inhomogeneities in a superconductor are known to influence its behavior, probably owing to a resulting spatial variation of the surface energy of a normal-superconducting boundary, it is the purpose of this Letter to propose a simplified model for the magnetic behavior of a homogeneous strain-free superconductor, in which a spatially independent negative surface energy could lead to large values of H_c^*/H_c.

Suppose that a superconductor of negligible demagnetizing coefficient divides itself, in the presence of a magnetic field H, into thin normal and superconducting laminas, of thickness d_n and d_s, respectively. Let us add to the resulting expression for g, the Gibbs free energy per unit volume,[3] an additional contribution arising from a configurational interphase surface energy, $\Delta' H_c^2/8\pi$. One then obtains

$$g=(H_c^2/8\pi)\left\{-x\left[1-\frac{q}{p}-h^2\left(1-\frac{\tanh p}{p}\right)\right]-h^2\right\}, \qquad (1)$$

where $H_c^2/8\pi$ is the difference in free energy per unit volume between the normal state and the superconducting state in zero field, $h=H/H_c$, $x=d_s/(d_n+d_s)$ is the fraction of the specimen in the superconducting state, $p=d_s/2\lambda$, and $q=\Delta'/\lambda$, λ being the penetration depth of the magnetic field. Equation (1) supposes that the London equation is obeyed in the superconducting laminas, a hypothesis we shall comment on later. As London pointed out,[3] the condition for Eq. (1) to lead to the well-known magnetic behavior of a so-called ideal superconductor is that $q>1$. Hence $\Delta=\Delta'-\lambda$, the total surface energy usually measured experimentally, is then positive. Pippard[4,5] has suggested that Δ' should be of the order of ξ, the coherence distance in the superconducting state. For pure superconductors, ξ tends towards a limiting value ξ_0 characteristic of the metal; while for very impure superconductors ($l\ll\xi_0$), ξ is of the order of l, the electronic mean free path.[6]

For $q<1$, corresponding to a superconductor of negative total surface energy, Eq. (1) leads to the existence of two transition fields. For h less than the lower transition field h', given by $h'=q^{1/2}$, one finds $x=1$ and $p=\infty$, so that here the specimen exhibits a Meissner effect, while for $h>h''$, where h'' is given by

$$q=h''+(1-h''^2)\tanh^{-1}(h''^{-1}), \qquad (2)$$

the normal state is stable. For $q\ll 1$, Eq. (2) becomes $h''=2/3q$. For intermediate fields the laminar structure is stable, the thickness of the

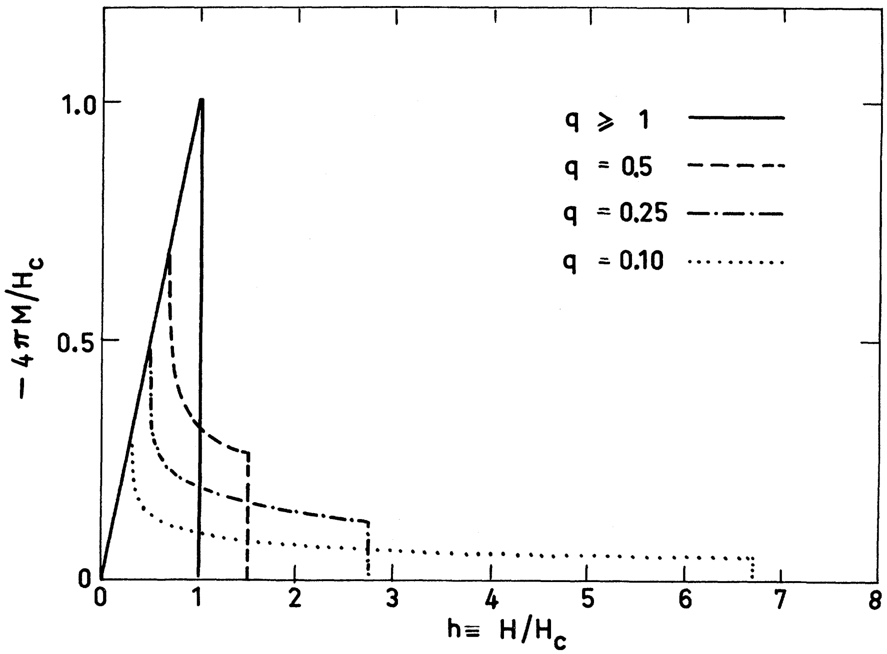

FIG. 1. Reduced magnetization curves for the present model of a superconductor, for different values of q.

superconducting laminas being determined by the equation $qh^{-2} = \tanh p - p\,\mathrm{sech}^2 p$, while that of the normal laminas remains negligible ($x = 1$). The magnetization M, given by $-4\pi M = xH[1-(\tanh p)/p]$, leads to the curves given in Fig. 1 for different values of q. We may note that, since the surface energy does not contribute to g either for $h = 0$ or for $h > h''$, the area under each magnetization curve is independent of q and satisfies the thermodynamic condition,

$$\int_0^\infty M dH = -H_c^2/8\pi.$$

It is tempting to correlate the prediction of two transition fields for $q < 1$ with the observation of Doidge[7] and Davies[8] that in dilute tin alloys the magnetic and resistive transitions become distinct when $l \lesssim \lambda$. However, the magnetic transitions observed by these authors went practically to completion at the lower transition field. The inadequacy of the present model, when l is not small compared with λ, is hardly surprising, since here the London equation is known to be inexact,[6] and furthermore it is physically unreasonable to assume, as we have done, that the normal laminas can be of negligible thickness.

However, these limitations should be much less serious for very impure superconductors, for which l is small, and Fig. 2 shows magnetization curves based on the present model which have been fitted to the hysteresis-free results obtained by Calverley and Rose-Innes[9] for a single mixed crystal of composition $Ta_{36}Nb_{64}$. It has here been assumed that the fields H_c^* quoted for the complete suppression of superconductivity correspond to the predicted discontinuous disappearance of M at h''. In fact, it is more probable that, owing to a field dependence of λ which we have not considered, the observed magnetization went to zero continuously, as has been found for superconducting thin films and colloids.[10,11] The results of these authors suggest that the effect of allowing λ to vary with H would probably be to distort the magnetization curves in Fig. 1 in such a way as (a) to yield a continuous disappearance of M, h'' being increased by at most a factor of about $\sqrt{2}$, and (b) to decrease the fitted values of H_c in Fig. 2 by not more than 10%. The correction required by the field dependence of λ has therefore been ignored.

By extrapolation of the values of H_c to 0°K one obtains $H_0 = 1600 \pm 100$ gauss, so that $H_0/T_c = 230$ gauss deg^{-1}, which is within 20% of the values found for this quantity for pure Ta and Nb. The value obtained for q, which is expected to be close to l/λ, may be discussed by using standard expressions relating λ, ξ_0, l/σ (σ being the conductivity of the specimen $= 2.5\times10^{-4}$ emu), and T_c (its transition temperature = 6.9°K) to the properties of the Fermi surface.[12] These lead to $\lambda = 800$ A

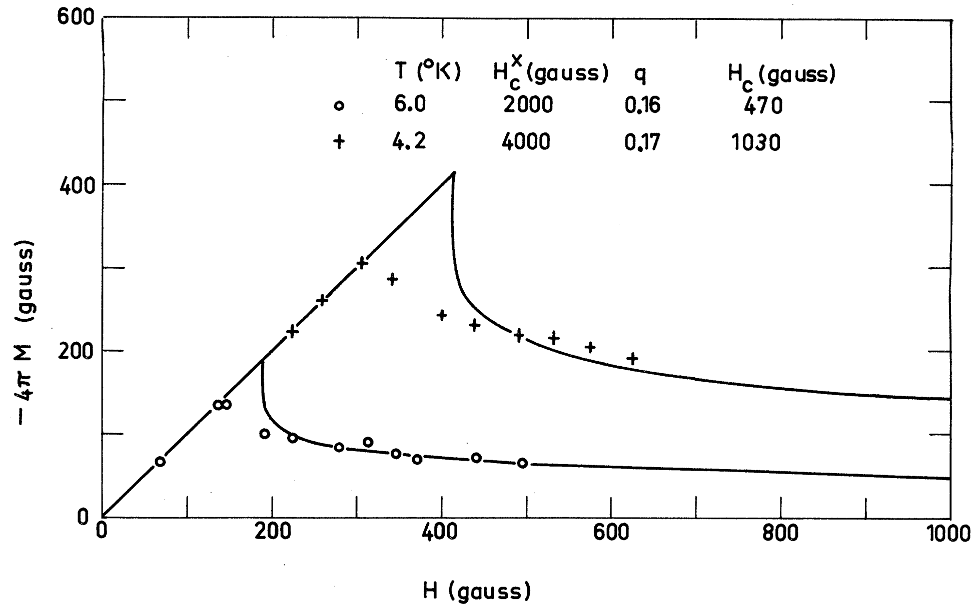

FIG. 2. Fit of the present model to the magnetization curves of Calverley and Rose-Innes' specimen of $Ta_{36}Nb_{64}$.

and $l = 76(S/S_0)^{-1}$ A, where S is the free area of the Fermi surface in the alloy and S_0 the area it would have if the five conduction electrons per atom were perfectly free. Thus the result $q = 0.16$ suggests that (S/S_0) should be somewhat less than unity, which does not seem unreasonable in view of the values of this order of magnitude which have been found for several other metals.[13]

The present model therefore seems to give a plausible account of the results of Calverley and Rose-Innes, and it confirms the impression that their magnetization curves represent a new type of magnetic behavior characteristic of homogeneous strain-free superconductors of negative surface energy. The magnetic field needed for the complete suppression of superconductivity, $h''H_c$, appears as a true thermodynamic variable, rather than as a property associated with certain individual lattice flaws. According to this model, for large h'', $h'' = 2/3q \approx 2\lambda/3\,\xi$, while using a different model, which takes into account the field dependence of λ, Pippard[5] finds a value which is only slightly larger: $h'' = (f\sqrt{6})\lambda_{H=0}/\pi\xi$; here f depends on the details of the model and lies between 1 and $\sqrt{2}$. Since for $l \ll \lambda$, we have $\lambda \propto l^{-1/2}$ and $\xi \approx l$, we may expect that, other things being equal, $h'' \propto l^{-3/2}$. The persistence of superconductivity in high magnetic fields, brought about by the existence of a negative surface energy, should therefore be favored by a short electronic mean free path, and thus a high resistivity, in the normal state.

[1]J. E. Kunzler, E. Buehler, F. S. L. Hsu, B. T. Matthias, and C. Wahl, J. Appl. Phys. 32, 325 (1961).
[2]J. E. Kunzler, E. Buehler, F. S. L. Hsu, and J. H. Wernick, Phys. Rev. Letters 6, 89 (1961).
[3]F. London, Superfluids (John Wiley & Sons, Inc., New York, 1950), Vol. I, pp. 125-130.
[4]A. B. Pippard, Proc. Cambridge Phil. Soc. 47, 617 (1951).
[5]A. B. Pippard, Phil. Trans. Roy. Soc. (London) 248, 97 (1955).
[6]A. B. Pippard, Proc. Roy. Soc. (London) A216, 547 (1953).
[7]P. R. Doidge, Phil. Trans. Roy. Soc. (London) 248, 553 (1956).
[8]E. A. Davies, Proc. Roy. Soc. (London) A255, 407 (1960).
[9]A. Calverley and A. C. Rose-Innes, Proc. Roy. Soc. (London) A255, 267 (1960).
[10]J. M. Lock, Proc. Roy. Soc. (London) A208, 391 (1951).
[11]C. S. Whitehead, Proc. Roy. Soc. (London) A238, 175 (1956).
[12]T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) A231, 336 (1955).
[13]R. G. Chambers, Proc. Roy. Soc. (London) A215, 481 (1952).