producibility to become more certain about this possible added scattering. In the 2 at.% bismuth sample, in which the electronic contribution to the total conductivity is larger, the effect seems to be more pronounced at the one temperature for which we have complete data. According to the Abrikosov model,[3] the spacing of the current vortices in the mixed state, at least near H_{c2}, is of the order of the superconducting coherence length, ξ. In our short mean free path alloys, $\xi \approx (\xi_0 l)^{\frac{1}{2}}$.[12] For indium, $\xi_0 \approx 2600$ Å[13] and for the 4 at.% Bi specimen the mean free path $l \approx 150$ Å, so that $\xi \approx 600$ Å.

To obtain an upper limit on the possible effect on the electronic conductivity we used the analysis of Strässler and Wyder[9] to calculate the difference between the conductivity parallel to and transverse to the vortex lines at the field corresponding to the empirical conductivity minimum, substituting in their expression the appropriate average field dependent energy gap. This predicted for the 4 at.% bismuth sample a difference in the total conductivity between the two orientations of about 12%. Using this method overestimates any possible effect, both because the electronic mean free path is in our case much smaller than the scale of the structure, and because the spatial modulation of the energy gap accompanying the vortex structure is probably not as effective a scatterer as an actual phase boundary. An effect of about 2% is thus not unreasonable, but we cannot be certain of its presence without further measurements with an improved technique.

[12] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 37, 1407 (1959) [English transl.: Soviet Phys.—JETP 10, 998 (1960)].
[13] A. M. Toxen, Phys. Rev. 127, 382 (1962).

ACKNOWLEDGMENTS

We are grateful to L. Del Vecchio for assistance in performing the experiments. One of us (H. R.) thanks Rutgers University and his colleagues for their hospitality during his most enjoyable and interesting stay.

Thermal and Magnetic Properties of Second Kind Superconductors. III. Specific Heat of Nb in a Magnetic Field*

T. MC CONVILLE and B. SERIN

Rutgers, The State University, New Brunswick, New Jersey

INTRODUCTION

Morin *et al.*[1] recently observed that V_3Ga in a magnetic field showed a specific heat discontinuity very similar to the discontinuity observed in most superconductors at the transition temperature in the absence of a field. Similar results for a specimen of Ta were obtained some years ago by Keesom and Désirant.[2] It was suggested by Goodman[3] that this behavior could be understood on the basis of the theory of Abrikosov.[4] According to this theory, in superconductors of the second kind the phase transition from the mixed state to the normal state at the upper critical field H_{c2} is a second-order transition. Both the entropy and the magnetization are continuous at the transition, but their derivatives are discontinuous. The discontinuity in the derivative of entropy gives rise to a specific heat discontinuity.

In this article we present observations on the specific heat of pure niobium in a magnetic field. Recently, on the basis of magnetic and resistance measurements,[5,6] this element has been identified as a superconductor of the second kind. The specific heat data which we have obtained do not seem to fit in a consistent way into the theory of Abrikosov.[4] Because of the great current interest in this field we pre-

* Research supported by the National Science Foundation and the Rutgers University Research Council.
[1] F. J. Morin, J. P. Maita, H. J. Williams, R. Sherwood, J. H. Wernick, and J. E. Kunzler, Phys. Rev. Letters 8, 275 (1962).
[2] W. H. Keesom and M. Désirant, Physica 8, 273 (1941).
[3] B. B. Goodman, Phys. Letters 1, 215 (1962).
[4] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [English transl.: Soviet Phys.—JETP 5, 1174 (1957)]; J. Phys. Chem. Solids 2, 199 (1957).
[5] T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters 9, 370 (1962); cf. also S. H. Goedemoed, A. van der Giessen, D. de Klerk, and C. J. Gorter, Phys. Letters 3, 250 (1963).
[6] S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters 9, 489 (1962).

sent these results despite the fact that this investigation is still in a very preliminary stage.

EXPERIMENTAL RESULTS

The niobium specimen was in the form of a cylinder 2.4 cm long and 0.6 cm in diameter, of mass 5.9 g (0.06 mole). It was prepared by electron beam melting in ultra-high vacuum by A. Calverley. We have as yet been unable to determine the resistivity of the specimen, but on the basis of its high transition temperature and small value of the Ginzburg–Landau parameter, κ, we believe that it is about as pure as any niobium specimen reported in the literature. The magnetic field was applied parallel to the cylinder axis of the specimen.

Details of the technique of the specific heat measurements will be presented elsewhere.[7] We mention at this time that no exchange gas was used, and that the heat pulses produced a temperature change of about 0.06°K. In Fig. 1 we show some of the results obtained in zero magnetic field and in a field of 1030 G. The numbers shown contain the heat capacity of the addenda so that they cannot be used to infer the absolute specific heat of the specimen. However, they are perfectly adequate for determining the temperatures at which discontinuities in specific heat occur, as well as the magnitudes of the discontinuities, since the contribution of the addenda subtracts out.

In zero field the specific heat curve has the expected form.[8] The transition occurs at $T_c = 9.19$°K, and the jump in specific heat is 1.51×10^4 erg/cm^3 (°K)^2. This value corresponds to a ratio of 2.22 between the jump and the normal state specific heat at T_c. From the magnitude of the specific heat discontinuity, the slope of the thermodynamic critical field at T_c may be calculated[9]; we obtain 434 G/°K.

From Fig. 1 we see that in a magnetic field the form of the specific heat curve depends on whether the field is applied before the specimen is cooled below T_c, or only after it has reached about 2°K. In the former case, the specific heat at low temperature is appreciably larger than in zero field and the discontinuity is relatively small. For the latter case, however, the specific heat values at low temperatures are indistinguishable from the zero-field values, but near the transition there is a very rapid increase in specific heat leading to an extremely large discontinuity. The areas up to T_c, under the curves of C/T, as a function of the temperature T (where C is the heat capacity), are about the same in both cases and agree to within a few percent with the area under the similar curve in zero field. Thus the total entropy change in going from 0°K to the transition temperature appears to be the same in all three cases.

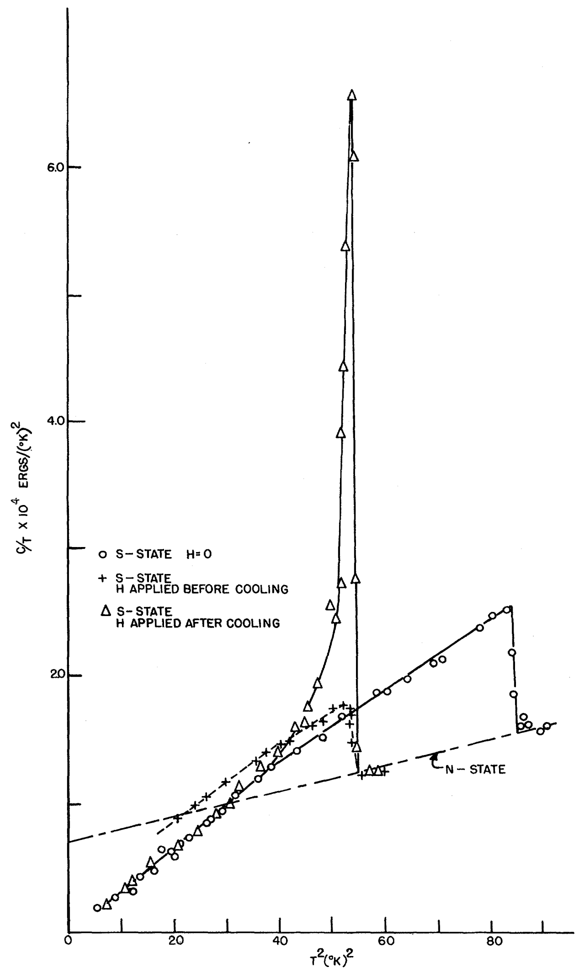

Fig. 1. The heat capacity divided by the absolute temperature is shown as a function of the square of the temperature. The applied field was 1030 G. The normal (N) state curve is extrapolated from data obtained at higher temperatures but not shown. To convert the jumps in heat capacity to the magnitudes of discontinuity in specific heat, the former are divided by the sample volume 0.681 cm^3.

Although it is not clear that this type of description is adequate, we tentatively analyze the data taken in a magnetic field in terms of a specific heat discontinuity, the magnitude of which we estimate. The behavior in a field may then be summarized as follows:

(a) In a field of 1030 G, applied after cooling below

[7] B. Serin and T. McConville, Calorimetry Conference, Bartlesville, Oklahoma, 1963 (unpublished).

[8] A. T. Hirshfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

[9] Cf. A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1957), p. 129, for a discussion of the superconducting transition and of higher-order transitions in general.

TABLE I. Summary of observations and calculations concerning the specific heat discontinuities. In cases (a) and (c) the magnetic field was applied after cooling to 2.2°K; in case (b) before cooling below T_c.

Case	Applied H (G)	$\langle T\rangle$(°K)	H_c (G)	$\kappa = 2^{-\frac{1}{2}} H_{c2}/H_c$	$\Delta C_p/T \times 10^4$ [erg/cm³(°K)²] (obs)	(calc)	κ^*
(a)	1030	7.30	719	1.01	7.94	2.06	0.80
(b)	1030	7.30	719	1.01	0.85	2.06	1.33
(c)	1470	6.59	966	1.07	4.60	1.65	0.86

2°K, the transition occurs at 7.30°K and the jump in specific heat is 7.94×10^4 erg/cm³(°K)².

(b) If the same field is applied before cooling below T_c, a jump of only 0.85×10^4 erg/cm³(°K)² occurs at the same temperature.

(c) A specific heat curve of shape similar to the one described in (a) was obtained in a field of 1470 G applied after cooling to the lowest temperature. In this case the transition occurs at 6.59°K with a specific heat jump of 4.60×10^4 erg/cm³(°K)².

DISCUSSION

In order to evaluate the data, the thermodynamic critical field H_c must be estimated at the temperatures at which the transitions occur in a magnetic field as evidenced by the jumps in the specific heat. We assume a parabolic critical field curve with a critical field at 0°K, $H_0 = 1990$ G. This value[10] gives a slope at the critical temperature equal to the value calculated from the jump in specific heat in zero field at T_c. The values of H_c at 7.30° and at 6.59°K calculated in this way are listed in Table I.

It is clear from the table that the applied field is appreciably larger than the critical field at the same temperatures, so that we must assume that at the temperature in question the applied field equals the upper critical field, H_{c2}. Thus one can use these data to find the Ginsburg–Landau parameter κ from the relation[4]

$$H_{c2} = 2^{-\frac{1}{2}}\kappa H_c\,. \tag{1}$$

The two values of $\kappa \sim 1$ obtained in this way agree with those already obtained from magnetic determinations[5,6] of H_{c2}. The slight increase in κ as the temperature decreases is also expected.

Moreover, when a field of 1030 G is applied after cooling to 2.2°K, the specific heat curve first deviates at about 5.46°K from the curve obtained in zero field. At this temperature, $H_c = 1285$ G, so that it seems appropriate to identify the applied field with the lower critical field H_{c1} in this case. We obtain a ratio $H_{c1}/H_c = 0.80$ at this temperature, which is not inconsistent with the data of Stromberg and Swenson.[5] It is interesting to note that the specific heat in a field shows a slow and continuous change in the neighborhood of the lower critical field.

The large abrupt changes in specific heat can be discussed in terms of the theory of second-order phase transitions,[3,8] combined with Abrikosov's expression[4] for the slope of the magnetization curve at the upper critical field, H_{c2}. These give for the discontinuity in specific heat at H_{c2}:

$$\frac{\Delta C_p}{T} = \left(\frac{dH_{c2}}{dT}\right)^2 \left(\frac{\partial M}{\partial H}\right)_T = \frac{(dH_{c2}/dT)^2}{[4.72\pi(2\kappa^2 - 1)]}\,, \tag{2}$$

where $(\partial M/\partial H)_T$ is the slope of the magnetization curve.

Assuming that H_{c2} varies linearly with temperature, we obtain from the data that $dH_{c2}/dT = 565$ G/°K. Thus from the values of κ already deduced, we can calculate from (2) the specific heat discontinuities to be expected. The calculated values are shown in Table I along with the observed values of $\Delta C_p/T$.

As can be seen from Table I, for case (b) where the field was applied before cooling below T_c, the observed jump in specific heat is much smaller than calculated. However, in the cases where the field is applied only after the specimen is cooled to the lowest temperature, the observed specific heat jumps are very much larger than the values calculated from (2). We tend to favor the data obtained when the field was applied only after cooling as representing the equilibrium states of the specimen. This feeling is based on the fact that we think that a specimen having a negative surface energy will be unlikely to completely expel a magnetic field when it is cooled below T_c. In such circumstances we would expect the specimen to exist in some sort of mixed state at all temperatures, which would explain a specific heat somewhat larger than the zero-field values at temperatures for which the applied field is less than H_{c1}. However, as is discussed below it is also possible that

[10] Stromberg and Swenson (Ref. 5) obtain $H_0 = 1960$ G. A crude graphical double integration of the specific heat curve in zero field yields $H_0 = 2200$ G. Even this largest value cannot remove the discrepancies in Table I.

the data taken with the field applied after cooling are characteristic of a nonequilibrium situation.

Returning to the large specific heat jumps, we see that if Eq. (2) is to give agreement with the observations, a larger value of $(\partial M/\partial H)_T$ is required at H_{c2}. In order to emphasize this point, we show in Table I, κ^*, which are the κ values required in order for Eq. (2) to agree with the measurements. There is a clear contradiction with those derived from (1). This result is most surprising since Stromberg and Swenson[5] find that experimentally the slope of the magnetization curve at H_{c2} is much smaller than that given by Abrikosov's expression. Thus we are left with a contradictory situation. Since we estimate our experimental accuracy as a few percent, we cannot trace the discrepancies to this cause.

In conclusion we outline several possibilities which have occurred to us as ways of resolving the dilemma presented by the data:

(i) It is conceivable that the observations are caused by some systematic error in the measurements in a magnetic field of which we are unaware.

(ii) The specimen does have an unfortunate shape. An ellipsoid of the same dimensions would have a demagnetizing coefficient of 0.08. Generally speaking we expect demagnetization effects to broaden any transition. However, it is conceivable that the sharp corners result in a nonequilibrium magnetization curve, even when the field is applied after cooling. If the curve corresponded to a larger than expected moment in fields exceeding H_{c1}, the slope at H_{c2} could be bigger than under equilibrium conditions, explaining the apparently too large specific heat jump.

(iii) It is possible that there is a latent heat of transition which would mean that the large jump does not correspond to a real change in specific heat. Under the circumstances, the transition would be first-order (occurring it is to be noted at about $1.4H_c$) and the foregoing analysis would not apply. However, we see no evidence for this possibility in the course of the experiments. When heat is supplied to the specimen, there are no intervals over which the temperature remains constant while latent heat is absorbed. Rather, the temperature continues to change so long as heat is supplied, but at a slower and slower rate as the specific heat peak is approached.

(iv) These qualitative observations suggest the possibility that the transition is a λ point with an infinite specific heat at the transition. In this connection, we note that decreasing the temperature intervals over which the specific heat was measured from 0.06° to 0.03°K, resulted in a 25% increase in the maximum value of the measured specific heat.

The situation clearly requires more detailed specific heat measurements, as well as magnetization and resistance measurements. Measurements on Nb–Ta alloys are also in progress.

Note added in proof. We have recently also measured a 95% Nb-5% Ta specimen, and a 50% Nb-50% Ta specimen. The values of κ for these specimens are, respectively, 1.62 and 4.24. In a magnetic field the 5% alloy showed an extremely large, sharp specific heat peak similar to the peak observed in pure Nb. However, the 50–50 alloy behaved in a field just as would be expected from theory. The magnitude of the observed specific heat discontinuity is in good agreement with the value calculated from Eq. (2).

ACKNOWLEDGMENTS

We are most grateful to A. Calverley and Dr. A. C. Rose-Innes, of the Services Electronics Laboratory, Baldock, Herts, England, who made this investigation possible by the loan of specimens. H. Fenichel devised several programs for computing the data. It is also a pleasure to acknowledge the help of Professor E. A. Lynton in preparing the manuscript.

Discussion 15

Autler: We have some measurements of κ_0 as a function of temperature, which will be reported tomorrow. It is of interest that your value falls exactly on our curve. These were obtained resistively.

J. F. Cochran, *Massachusetts Institute of Technology:* In the curves you showed of the specific heat of niobium, in which you had cooled the specimen at zero field and measured the specific heat in a field, you got a large peak in the specific heat. That looks very much like a latent heat. Would you please comment on that.

Serin: This is a possibility we have considered. Unfortunately it is somewhat contradictory since the field where the specific heat peak occurs is larger than the critical field. The only possible explanation I have come up with in discussion with other people is that perhaps the niobium κ is so close to the critical value that the specimen is partly first kind and partly second kind—perhaps on a very fine scale. It would be the first kind that's giving this tremendous peak that we cannot explain any other way. If that were true, this would mean that pure niobium was a first-kind superconductor and the whole business should not apply. The other possibility is that the Abrikosov theory does not apply for other reasons, mainly that the mean free path is rather long; but then we're in trouble with the magnetization. We cannot get a slope that would give consistent agreement. So the situation, although in a muddle, seems rather interesting to us.

J. A. HULBERT, *Royal Radar Establishment:* I just want to make a remark in connection with Dr. Lynton's remarks on the puzzle about the Shapoval and the Gor'kov theories and their relative ranges of validity. We have measured some niobium–zirconium wires and looked at the upper part of the transition where the last part of the normal resistance had just returned. In these circumstances, we observe a positive curvature in the relation between the critical field and the temperature, down to temperatures of half the critical temperature. The amount of curvature is a function of the value of kappa. The interesting thing about these results is when we work out the thermodynamic critical field using Shapoval's relations we obtain results which are very close to those obtained by direct measurement (Blaugher and Hulm, for example) on the 25% zirconium alloy. The values of kappa obtained near T_c and from the zero-temperature extrapolation using the Shapoval theory again are extremely close, within 10%. It appears from these results that the curvature changes from positive to negative at a kappa of about 20. Similar results on lead–bismuth (eutectic alloy) which have a kappa value lower than 20 fit into the general picture. It appears that the critical field defined by the restoration of full normal resistance is not inconsistent with both Gorkov and Shapoval theories in their stated ranges of validity.

WERTHAMER: I've re-examined Shapoval's derivation and find that although he seems, in principle, to proceed along correct lines, there's a serious algebraic error at a rather crucial stage in the calculation. In a preliminary attempt to repeat the calculation with the error corrected, I find that the mean free path drops out of the final expressions. This is well-known to be true in the limit of vanishing magnetic field, but is contradicted by Shapoval's formulas. It appears that Gor'kov's result holds independent of the mean free path.

Mean Free Paths in the Normal and the Superconducting State

P. WYDER
Swiss Federal Institute of Technology, Zürich, Switzerland

Until now, no direct measurements of the mean free path of the excited electrons in a superconductor have been made. The purpose of this investigation is to determine experimentally the mean free path of indium in the superconducting state by size effect measurements of the thermal conductivity, and to compare it with the mean free path of the electrons in the normal state. Our results indicate that in the limit of the precision of such size effect measurements these two mean free paths are equal.[1]

If the mean free path is comparable to the dimensions of the specimen, there will be an additional scattering of the electrons at the boundaries. This gives an additional term in the resistivity. If one assumes that the thermal conductivity is proportional to the mean free path l, and that all electrons are scattered diffusely at the surface of the specimens, one has for the thermal resistance $W(d)$ of a cylindrical wire of diameter d according to a qualitative argument due to Nordheim[2]

$$W(d) = W_\infty(1 + l/d) .$$

W_∞ represents the thermal resistance of an infinitely thick specimen. This formula agrees very well with Dingle's[3] exact solution. Now it is possible to determine the mean free path for the thermal conductivity by measuring the thermal resistance of wires with several thicknesses and by fitting the experimental data either to Nordheim's formula or to Dingle's table, using W_∞ and l as parameters.[4] This can be done both in the normal and in the superconducting state. In this manner, the mean free paths in the two states are determined. The measurements have been carried out on indium of remarkably high purity, where, in the temperature range investigated, the heat conductivity due to phonons can entirely be neglected compared with the conductivity due to electrons. The specimens were extruded very carefully through nozzles made from sapphire, and self-annealed at room temperature for several weeks. Superconductivity was quenched with a longitudinal magnetic field, and the resultant magnetoresistance of several percent was corrected either by Kohler's rule or by using a quadratic extrapolation.

In Fig. 1, the measured thermal resistance W in the normal and in the superconducting state is plotted as a function of the temperature T for several wires of different thicknesses. The ratio W_n/W_s is independent of the thickness and in good agreement

[1] For preliminary results of this investigation, see P. Wyder, Phys. Letters **5**, 301 (1963).
[2] L. Nordheim, Acta Sci. et Ind. No. 131, Paris (1934).
[3] R. B. Dingle, Proc. Roy. Soc. (London) **A201**, 545 (1950).
[4] J. L. Olsen and P. Wyder, Helv. Phys. Acta **32**, 311 (1959).