

Specific Heat of Aluminum Near its Superconductive Transition Point

By DAVID C. RORER, HORST MEYER *, and ROBERT C. RICHARDSON

Department of Physics, Duke University, Durham, N.C., U.S.A.
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Dedicated to Prof. Dr. K. CLUSIUS on his sixtieth birthday

We have carried out specific heat measurements with a high temperature—resolution in different magnetic fields on three cylindrical specimens of aluminum. The experiments were confined to the region of the critical field curve between 1.1 and 1.2 °K and were carried out with a sensitive calorimeter in which temperature changes of $\sim 1.5 \times 10^{-4}$ °K could be determined to about 2%. These measurements gave the difference of the specific heat between the superconductive and the normal state, the latent heat and the critical field curve. For a reversible transition, these three quantities are related by thermodynamic equations and hence it is possible to check their consistency. For one sample, this consistency was within experimental error and we obtained the slope $(dH_c/dT)_{H=0} = -153$ gauss/degree. For the two other samples, there was some slight systematic disagreement between the critical curve as measured and as calculated. The shape of the transition in zero field has been investigated in detail and it was found that the phase change could take place within about 0.6×10^{-3} °K for one sample, while for the two others it was spread over two millidegrees. From the width we have estimated the correlation range using PIPPARDS theory. The critical temperature in zero field was found to be respectively 1.173, 1.183 and 1.188 °K and no λ anomaly in the specific heat, as discussed in recent theories could be detected at the transition.

Of the better investigated superconductors, aluminum seems to show the largest scatter in its superconductive properties, as measured for different samples and in different types of experiments. The transition temperature in zero field T_{co} , for example, is shown to vary between 1.16 °K¹ and about 1.20 °K², while the slope of the critical field curve, $(dH_c/dT)_{H=0}$, varies between about -150 gauss/degree, as determined from specific heat data, and

about -180 gauss/degree if measured magnetically. For tin and indium, on the other hand, the results are consistent^{3, 4}. Some of the more recent values of T_{co} and $(dH_c/dT)_{H=0}$ for aluminium are given in Table 1. The variations might well arise partially because of difficulties in accurate temperature measurement in the 1 °K region. More probably they might be due to differences in the purity, the crystalline condition and the shape of the samples. Because of the discrepancy in the (dH_c/dT) data it seemed necessary to check if, for one particular sample at least, the properties related by the well-known thermodynamic equations¹⁰ were internally consistent, that is if the superconductive transition was a reversible one. Hence it was decided to measure these properties simultaneously on the same specimen. At the beginning of this work, such an experiment had not, to our knowledge, been carried out on any superconductor. Calorimetric measurements were thought suitable since they were able to determine $C_s - C_n$, L , and the critical curve in the same experiment and hence permit a consistency check.

T_{co}	$(dH_c/dT)_{H=0}$ (gauss/degree)	Method	Author
1.197 *	- 177	Magnetic	GOODMAN et al ⁵
1.172 *	- 164	Magnetic	FABER ⁶
1.174 *	- 163	Magnetic	MUENCH ⁷
1.196	- 165	Magnetic	COCHRAN et al ⁸
1.162	- 152	Calorimetric	PHILLIPS ¹
1.19	~ - 150	Calorimetric	GOODMAN ⁹

* Temperatures according to the 1949 Helium vapour scale. Earlier data are compiled in LANDOLT-BÖRNSTEIN, 2nd Volume, Part 6, p. 110, Verlag Springer, Berlin 1959.

Table 1.

* Alfred P. Sloan Fellow.
¹ N. E. PHILLIPS, Phys. Rev. **114**, 676 [1959].
² J. F. COCHRAN, D. MAPOTHER and R. E. MOULD, Phys. Rev. **103**, 1657 [1956].
³ D. MAPOTHER, Phys. Rev. **126**, 2021 [1962].
⁴ D. K. FINNEMORE, Thesis, University of Illinois 1962.
⁵ B. B. GOODMAN and E. MENDOZA, Phil. Mag. **42**, 594 [1951].

⁶ T. E. FABER, Proc. Roy. Soc., Lond. **A 231**, 353 [1955].
⁷ N. L. MUENCH, Phys. Rev. **99** 1814 [1955].
⁸ J. F. COCHRAN and D. MAPOTHER, Phys. Rev. **111**, 132 [1958].
⁹ B. B. GOODMAN, C. R. Acad. Sci., Paris **224**, 2899 [1957].
¹⁰ See for example D. SCHOENBERG, Superconductivity, Cambridge University Press 1952.



Here C_s and C_n are respectively the specific heat per mole in the superconductive and in the normal state and L is the latent heat of transition in a magnetic field H_c . In practice, the transition of a superconductor is not infinitely sharp and the latent heat manifests itself by a specific heat bump whose integration over the transition region gives L .

In this paper we shall describe specific heat measurements with high temperature resolution on three aluminum samples. They were carried out in "zero" field* and in several fields up to 10 gauss in the region immediately around the transition curve between 1.1 and 1.2 °K. The temperature shift of the specific heat bump with the magnetic field gave the critical curve as will be described below. Emphasis was given to the determination of the transition shape in "zero" magnetic field for the different samples. It was of course expected that samples of different preparation would show different transition widths but it was hoped that the purest annealed sample would give a very sharp transition. Lastly the experiments were carried out in order to determine whether the specific heat near the transition point in zero field would show a λ -type increase, as discussed by KVASNIKOV¹¹ and by BUCKINGHAM and FAIRBANK¹².

Experimental

The principle of the specific heat measurements consisted in recording continuously the temperature change of the sample as a function of time for a constant heat input. In studying the intermediate region this way, it was necessary to warm up the sample very slowly. This was required not only by the need to have a uniform temperature throughout the sample but also by the time constant of the sensitive temperature recorder. The sample thus had to be well-insulated thermally from the surroundings. Hence a mechanical heat-switch technique which avoids the need of helium exchange gas had to be used. Fig. 1 shows schematically the cryostat with a heat switch similar to that described BUCKINGHAM and FAIRBANK¹². The liquid helium in the pot F could be cooled by forced evaporation down to about 0.9 °K and the vapour pressure was measured via a special manometer line B. This tube ended within 2 cm. of the helium pot and calculations showed that for the pump-

ing rate used, the pressure gradient between the surface of the liquid and the manometer line was less than 0.1% of the measured pressure. In order to secure good thermal contact between the copper container and Helium II, bundles of copper wire filled this container and were hard-soldered to its walls. Solder connections nearest the sample were made with a Cd-Bi eutectic solder which does not become superconductive above 1 °K.

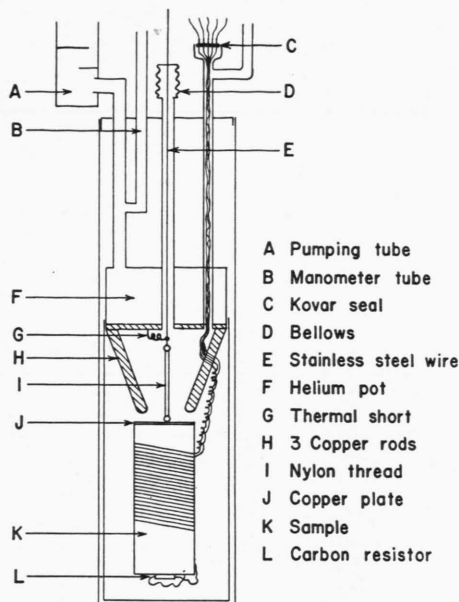


Fig. 1. The cryostat with the aluminum sample, shown schematically. The top of the apparatus and the surrounding DEWAR, containing liquid helium at 4.2 °K, have been omitted.

The measurement of the vapour pressure of Helium 4 between 1.3 and 1.0 °K is somewhat more delicate than at higher temperatures. We have used an oil manometer, calibrated to better than 1% against a mercury manometer in every experiment and we compared its readings with those of a McLEOD gauge. Between 1.2 and 1.4 °K, these two instruments agreed within about 1%. Below 1.17 °K, only the McLEOD gauge was used and from the consistency of successive readings the pressure could be determined to 1% or better. The vapour pressure tables of 1958¹³ were used to convert the pressure readings into temperature, appropriate corrections being taken for thermomolecular effects¹⁴. We estimate that the temperature of the individual points was known at least within 10^{-3} °K, according to this scale.

* (< 0.003 gauss).

¹¹ I. A. KVASNIKOV, Dokl. Akad. Nauk SSSR. **119**, 475 [1958]; Translation: Soviet Phys. Doklady **3**, No. 2 p. 318 [1958].

¹² M. J. BUCKINGHAM and W. M. FAIRBANK, Progress in Low Temperature Physics, Vol. 3, p. 80, North Holland Pub-

lishing Company 1961; C. F. KELLERS, Thesis, Duke University 1960.

¹³ H. VAN DIJK, M. DURIEUX, J. R. CLEMENT and J. K. LOGAN, National Bureau of Standards Monograph 10 [1960].

¹⁴ T. R. ROBERTS and S. G. SYDORIAK, Phys. Rev. **102**, 304 [1956].

For the heat switch, a thin copper disk J with a hook was glued with a small amount of epoxy resin to the top face of the aluminium cylinder, which hence could be pulled by a nylon string against three copper tusks H. The fact that the coefficients of expansion of Al and Cu are reasonably close¹⁵ made us hope that the strain on the top of the specimen during the cooling would not be too large. A drop of about 0.2 mm^3 of pure indium was hanging from the bottom of each tusk in order to improve thermal contact when the heat switch was closed. It was estimated that this indium only negligibly influenced the distribution of the magnetic field around the sample. Sufficient thermal contact was reached by only slightly pulling on the stainless steel wire and the sample warmed up less than one millidegree when one opened the switch carefully. The temperature drift of the sample was then very small, corresponding to heat leaks of the order of $.01 \text{ ergs/sec}$, which showed that there was little effect from vibrations.

The heater was made from Formvar-insulated Manganin wire of about 2000Ω and was wound bifilarly on the sample and glued to its surface by a thin layer of varnish. Little strain should come from the winding of the heater around the sample, since the aluminium contracts more than the manganin upon cooling. The heater was brought through leads of about 2 Ohms to the Helium container where they were thermally anchored and then brought through a Kovar seal C into the 4.2°K Helium bath, from there to the controls.

The carbon resistor L for the temperature measurement was a $62 \text{ Ohm } 1/10 \text{ watt}$ Allen Bradley resistor, glued inside a thin copper sheath which in turn was glued to the bottom of the sample. Its resistance was measured by using a 10 cycle WHEATSTONE bridge connected to a high-gain tuned commercial amplifier and a phase-sensitive detector. The offbalance signal was then fed into a Leeds and Northrup chart recorder. The power input into the resistor was between 0.005 and 0.010 ergs/sec . As was pointed out by COCHRAN¹⁶, the sensitivity of a WHEATSTONE bridge, when expressed as the minimum detectable change in temperature is almost insensitive to the resistance of the thermometer. At 1.17°K , the resistance was about $45,000 \Omega$ and the change with temperature was about $2 \times 10^5 \text{ ohms/degree}$. By averaging over the noise pattern on the chart recorder, changes in temperature of the order of $1.5 \times 10^{-4}^\circ \text{K}$ could be determined to about 2%. Individual specific heat points could then be calculated to about 3%. Hence the accuracy of our measurements was appreciably less than that achieved in high precision calorimetry¹⁷ where larger temperature intervals and a larger power input into the thermometer are used for each specific heat point.

The calibration of the thermometer was done for about thirty points between 1.05 and 1.3°K before and after the series of heating periods. The sample was

then in thermal contact with the helium bath through the heat switch. These calibration points were taken only when no temperature drifts larger than about 0.2 millidegrees over a period of several minutes were noticed. The curves so obtained on different runs almost coincided, showing that between the different experiments the carbon resistor had almost not changed its resistance curve, even if it had been warmed up to room temperature.

While the whole apparatus was initially being cooled to liquid helium temperatures, the magnetic field from the earth and the surrounding metal systems was compensated to better than 3×10^{-3} gauss within a radius of almost 5 cm from the center of the sample. This was achieved by two mutually perpendicular sets of HELMHOLTZ coils placed around the cryostat and the compensation was periodically checked by an air-driven rotating coil, the voltage signal of which was displayed on an oscilloscope. A long solenoid surrounding the cryostat was used to apply a steady magnetic field to the sample parallel to its axis. It was calculated that the field was homogeneous to 0.2% over the aluminum rod.

Heating the sample through the intermediate region was done either at constant field while the increase of the temperature was recorded as a function of the time or it was done at constant temperature while the field was increased from zero to H_c . The first method was the one most commonly used in this work. The sample was first cooled in "zero" field to a temperature about ten or fifteen millidegrees below the chosen transition point. The heat switch was then opened and the drift rate of the temperature was checked. By holding the temperature of the helium pot slightly below that of the sample, the drift rate could be made very small. A magnetic field was then applied and its value was increased slowly enough to prevent eddy current effects until one was very close to the intermediate region. This region was not reached as long as the temperature of the sample did not decrease with increasing field due to adiabatic magnetization. The sample was then slowly heated through the transition, drift rates being taken approximately every five minutes to check possible changes in stray heat leaks and to apply suitable corrections for the calculation of the specific heat. Usually it took about twenty minutes to heat the sample through the transition in zero field with a power input of about 0.8 ergs/sec . In a field of 10 gauss, where the latent heat is rather large, the heat input had to be increased to about 10 ergs/sec to keep the time necessary to complete the transition below one hour. Calculations showed that for the largest heating rates used, the temperature was still homogeneous enough through the sample, the temperature difference between the surface and the axis being less than 10^{-6}°K . In the region of the specific heat maximum, the noise appearing on the chart recorder was appreciably larger than usual and this effect increased with the size of the applied field. A

¹⁵ D. BIJL and H. PULLAN, *Physica* **21**, 285 [1955].

¹⁶ J. F. COCHRAN, *Ann. of Physics* **19**, 186 [1962].

¹⁷ See for instance K. CLUSIUS, P. FRANZOSINI and U. PIESBERGEN, *Z. Naturforsch.* **15a**, 728 [1960] and K. CLUSIUS and C. G. LOSA, *Z. Naturforsch.* **10a**, 939 [1955].

careful check showed that this was not due to fluctuations of the applied field. It is possible that this noise may be due to jumps of superconductive domains into normal ones. By analysis of the specific heat data, C_s and C_n were determined and the latent heat was obtained by integration under the specific heat maximum as will be described in a later section.

The method of isothermal heating, on the other hand, gave the latent heat directly. As in the first method, the sample was cooled in zero field, the heat switch was opened and the field was increased slowly until there was a just perceptible cooling of the sample: one was then at the threshold of the intermediate state. After reducing the temperature drift to practically zero, the heat was switched on and the field gradually increased to keep the temperature constant. At a certain moment, a change of field could no longer influence the temperature. The transition was then complete, the heat was immediately stopped and the temperature T_c , the heat input, and the final field were recorded. Such an operation took up to twenty minutes, the temperature fluctuations being kept below 2×10^{-4} °K. The error in this determination of L was estimated to be between 1 and 2%.

In order to check if supercooling took place, we have also measured the specific heat by cooling the sample slowly through transition in zero field. During this process, as a check, heat was periodically switched on so as to balance the cooling rate of the sample. If then the drift rate had not changed from one check to the other, it meant that the cooling rate had remained constant.

The Specimens

The aluminium samples were all provided by Dr. D. SERAPHIM of the I. B. M. Research Laboratories, and they were analysed spectrographically by the Detroit Testing Laboratory. The analysis and the dimensions are shown in Table 2. All three specimens had been annealed in vacuum at 600 °C for 12 hours. Samples I and II were originally part of the same cylinder of aluminium with a nominal purity of 99.99%. Al-I was zone-refined. Surface etching showed that this cylinder was made up of two large single crystals with a volume ratio of roughly 4 : 1.

Al-II contained the impurities removed from sample I by zone refining and was shown to consist of about six single crystals of roughly equal size.

The sample Al-III was polycrystalline, the grains being of the order of 1 mm³, as shown by surface etching. Cooling a polycrystalline sample should not introduce strains, since aluminum is cubic and the coefficient of expansion should be isotropic. Hence at low temperatures, a polycrystalline sample should have no more strains than large single crystals.

Impurity content	Al I	Al II	Al III
Cu	< 0.0008%	< 0.0005%	< 0.0005%
Fe	< 0.0006	< 0.0005	< 0.0005
Si	0.009	0.01	0.009
Mn	0.0003	0.001	0.001
Mg	0.001	0.002	0.004
Ti	—	0.0005	0.0005
Ni, Cr, Pb, Bi, Sn and Ag not detected.			
<i>Dimensions</i>			
Length	6.40 cm	7.04 cm	6.38 cm
Diameter	1.75 cm	1.78 cm	1.90 cm
Mass	41.827 gr	45.653 gr	47.244 gr

Table 2. Purity and shape of the aluminum specimens.

Although admittedly our specimens were not ellipsoidal, it still seemed reasonable to define for them a demagnetization factor n with the same value as for an ellipsoid with the axis ratio equal to the ratio of diameter-to-length for the cylinder. Hence we calculated for our samples I, II, and III demagnetization factors respectively equal to 0.085, 0.077 and 0.094.

Results and Analysis of the Data

A) Specific heat in zero field

The results are presented in Fig. 2, and the data for the three samples are given in Table 3. Addenda corrections for the copper disk, the resistor mounting, the heater and the glues were calculated to amount to less than 2% of the total heat capacity below the transition and were accordingly subtracted from the data¹⁸. C_s and C_n were found to agree satisfactorily with the data of PHILLIPS near the normal transition point. The small difference in the absolute values may be due to an error in the estimation of the addenda. However this is immaterial in this work, since we will be only interested in the difference of the specific heats below and above T_{co} . The value $C_s - C_n$ we find for all three samples is slightly higher than that of PHILLIPS¹ but agrees better with recent data of HOPKINS and MAPOTHER¹⁹. During a series of heatings through the transition in zero field, no temperature shift larger than say 10^{-4} °K of the specific heat curve could be observed.

¹⁸ A compilation of data and references on the specific heat of these addenda is found in the National Bureau of Standards Monograph No. 21: Specific Heats and enthalpies of technical solids at Low Temperatures (1960).

¹⁹ D. C. HOPKINS, Thesis, University of Illinois, 1962. — D. C. HOPKINS and D. MAPOTHER, Bull. Amer. Phys. Soc. 7, 175 [1962].

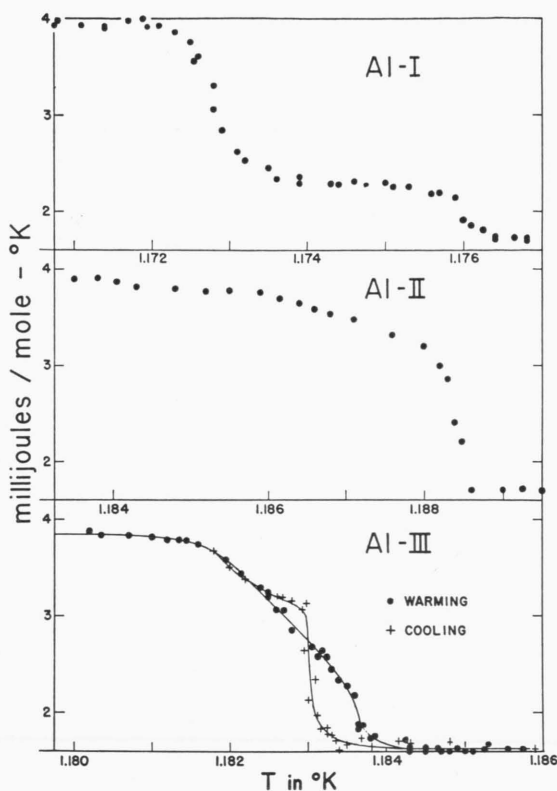


Fig. 2. The specific heat in "zero" field for the three samples. For Al III, the warming and cooling curves are indicated.

Surprisingly the specific heat for Al-I showed two successive sharp decreases at the transition point. Since there were two single crystals in this sample, and since their volume ratio was about the same as the ratio of the specific heat jumps, it was concluded that the two single crystals had transition temperatures differing by two millidegrees. For the larger crystal, the transition width was estimated by extrapolation to be about $6 \times 10^{-4}^\circ\text{K}$. In small magnetic fields, one could see two maxima of the specific heat due to the two crystals. In fields above 1 gauss, the smaller bump became smeared out, but the end of the transition for both crystals was still well established. For sample II, the transition started slowly over a range of about two millidegrees and became very sharp at the end. Such a transition shape was observed by HOPKINS and MAPOTHER¹⁹ on a single crystal. For Al III, the transition was continuous over about two millidegrees but a change in

the shape of the curve was observed when the sample was cooled through the transition. For Al I, no such a conclusive change of shape upon cooling was observed, and unfortunately no cooling data were taken for Al II. No λ -shaped heat capacity term could be detected for any of our samples near the transition temperature. This was to be expected from the discussion of BUCKINGHAM and FAIRBANK¹² that for a superconductor this term should be much smaller than for liquid helium. However it may also occur over such a small temperature interval that it cannot be measured by the present day techniques. A discussion of this question has been given by COCHRAN¹⁶.

B) Evaluation of the latent heat in a constant external field

Some of the specific heat data in magnetic fields are given for sample III in Fig. 3²⁰. For some fields two specific heat curves were taken which were found to be consistent. In the intermediate state, the total specific heat measured in a constant applied field H_e is given by¹⁰

$$C = x C_n + (1 - x) C_s - \frac{V T}{4 \pi} H_c \frac{dH_c}{dT} \frac{dx}{dT}. \quad (1)$$

Here x is the concentration of the normal phase and V is the molar volume. The third term on the right side is the heat required for the transformation from the superconductive to the normal state in a field H_c . In the intermediate state, the field H_c varies from approximately $H_c/(1 - n)$ to $H_c = H_e$ at the end of the transition. This third term was obtained from the total specific heat by subtracting the first two terms, for which C_s and C_n had been measured respectively below and above the transition and x had been determined by successive approximations from the specific heat shape. The third term was then integrated to give the latent heat, and the individual values so obtained were estimated to carry an uncertainty of 4% or less. It is gratifying that they agree within 3% with those obtained from isothermal heating measurements. The results are presented in Table 4. From the fraction of the latent heat used to reach a temperature in the intermediate state, the concentration x of the normal state was derived as a function of T , as has been done by

²⁰ A more complete tabulation of the data and other figures not shown here because of space considerations (in par-

ticular the data for Al I and Al II) will be given in the thesis of D. C. RORER.

<i>T</i>	<i>C</i>	<i>T</i>	<i>C</i>	<i>T</i>	<i>C</i>	<i>T</i>	<i>C</i>	<i>T</i>	<i>C</i>
Al I Run 1		Al I Run 2		Al II Run 1		Al III Run 2		Al III Run 1 (cooling)	
1.17080	3.98	1.17390	2.29	1.18830	2.86	1.18325	2.58	1.18180	3.69
1.17140	3.93	1.17430	2.29	1.18840	2.41	1.18365	1.84	1.18200	3.50
1.17195	3.92	1.17460	2.32	1.18850	2.21	1.18385	1.76	1.18220	2.28
1.17210	3.98	1.17500	2.30	1.18860	1.71	1.18430	1.65	1.18265	3.20
1.17230	3.97	1.17530	2.26	1.18900	1.70	1.18450	1.64	1.18295	3.06
1.17260	3.61	1.17560	2.19	1.18925	1.72	1.18470	1.64	1.18295	2.64
1.17280	3.31	1.17590	2.15	1.18950	1.70	1.18490	1.635	1.18300	2.14
1.17310	2.62	1.17610	1.86	1.19000	1.72	1.18520	1.63	1.18310	1.97
1.17350	2.45	1.17625	1.81			1.18555	1.63	1.18325	1.78
1.17390	2.36	1.17640	1.74	Al III Run 1		1.18575	1.62	1.18330	1.78
1.17440	2.28	1.17665	1.73	1.18250	3.20	Run 3		1.18340	1.62
1.17475	2.27	1.17680	1.72	1.18260	3.07	1.18020	3.88	1.18380	1.66
1.17510	2.26	1.17780	1.67	1.18270	3.04	1.18035	3.84	1.18430	1.53
1.17570	2.20			1.18280	2.87	1.18070	3.84	Run 2 (cooling)	
1.17600	1.92	Al II Run 1		1.18320	2.65	1.18120	3.82	1.18260	3.20
1.17640	1.72	1.18230	3.86	1.18330	2.56	1.18120	3.79	1.18210	3.16
1.17680	1.71	1.18300	3.91	1.18340	2.34	1.18135	3.79	1.18300	3.16
1.17730	1.71	1.18350	3.90	1.18350	2.28	1.18145	3.78	1.18310	2.35
1.17850	1.72	1.18380	3.91	1.18360	2.18	1.18160	3.74	1.18315	1.83
1.17890	1.71	1.18405	3.87	1.18370	1.87	1.18180	3.66	1.18325	1.85
Run 2		1.18430	3.82	1.18385	1.75	1.18195	3.58	1.18330	1.76
1.17070	3.95	1.18480	3.80	1.18430	1.60	1.18215	3.44	1.18335	1.70
1.17110	3.94	1.18520	3.77	1.18450	1.60	1.18250	3.25	1.18350	1.67
1.17140	3.90	1.18550	3.78	1.18470	1.60	1.18270	306.	1.18370	1.74
1.17170	3.98	1.18590	3.76	1.18490	1.60	1.18310	2.57	1.18380	1.74
1.17190	4.00	1.18615	3.70	1.18510	1.60	1.18330	2.45	1.18415	1.71
1.17210	3.93	1.18640	3.65	1.18525	1.61	1.18365	1.88	1.18430	1.69
1.17230	3.86	1.18660	3.59	Run 2		1.18425	1.72	1.18465	1.63
1.17250	3.76	1.18680	3.54	1.18240	3.30	1.18465	1.64	1.18480	1.70
1.17255	3.56	1.18710	3.48	1.18260	3.06	1.18530	1.67	1.18500	1.58
1.17280	3.06	1.18760	3.32	1.18280	2.85			1.18530	1.58
1.17290	2.85	1.18800	3.20	1.18305	2.68			1.18590	1.63
1.17320	2.53	1.18820	3.00						
1.17360	2.34								

Table 3. Specific heat, C , in millijoules/mole degree for the three samples, in zero field as a function of T . The temperature is given within 5×10^{-5} °K to show the resolution between the points. The *absolute* value of T is, of course, only known to about one millidegree.

Al I			Al II			Al III		
T_c	H_c	L	T_c	H_c	L	T_c	H_c	L
1.17340	0.000	0.00	1.18850	0.000	0.00	1.18380	0.000	0.00
1.17175	0.295	4.20	1.18585	0.295	3.28	1.18210	0.295	3.51
1.17060	0.491	6.00	1.18480	0.492	5.25	1.18050	0.492	6.35
1.16800	0.983	13.2	1.18280	0.790	8.45	1.17805	0.790	12.5
1.16490	1.47	19.5	1.18155	0.983	12.00	1.17715	0.983	15.4
1.15880	2.46	32.7	1.17475	1.98	26.8	1.17335	1.47	21.9
1.15540	2.94	40.6	1.17020	2.67	34.2	1.17000	1.97	30.7
1.14930	3.93	53.2	1.16420	3.54	45.7	1.16360	2.94	40.2
1.14325	4.92	68.0	1.16190	3.94	49.6	1.15730	3.93	57.9
1.12375	7.87		1.15825	4.42	57.4	1.15080	4.42	64.3
1.11180	9.80		1.15620	4.80	62.1	1.13790	6.87	
			1.14900	5.81	75.8	1.11820	9.80	128
			1.13755	7.56	100			

Table 4. Experimental critical field curve and latent heat L for the three samples. Here again, the temperature is given within 5×10^{-5} °K to show the resolution. L is expressed in microjoules per mole.

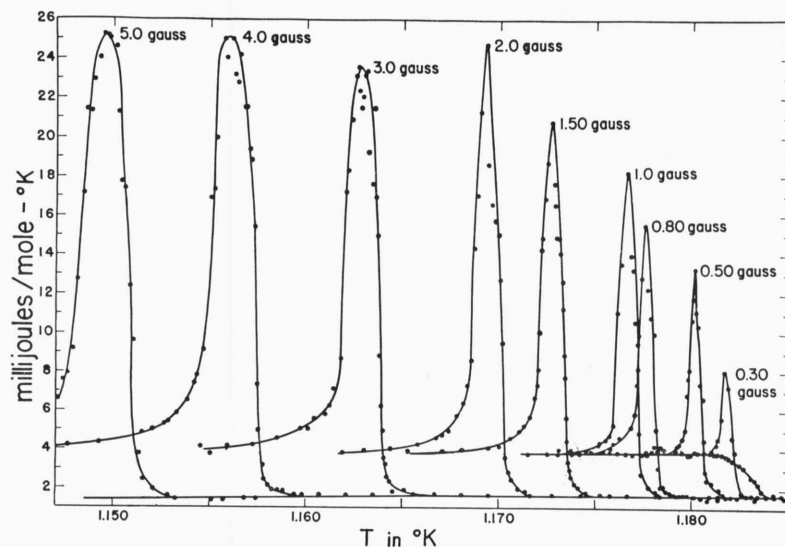


Fig. 3. The specific heat for sample Al III in fields up to 5 gauss. The sharpening of the transition when the field is increased from 0 to 0.3 gauss can be seen clearly.

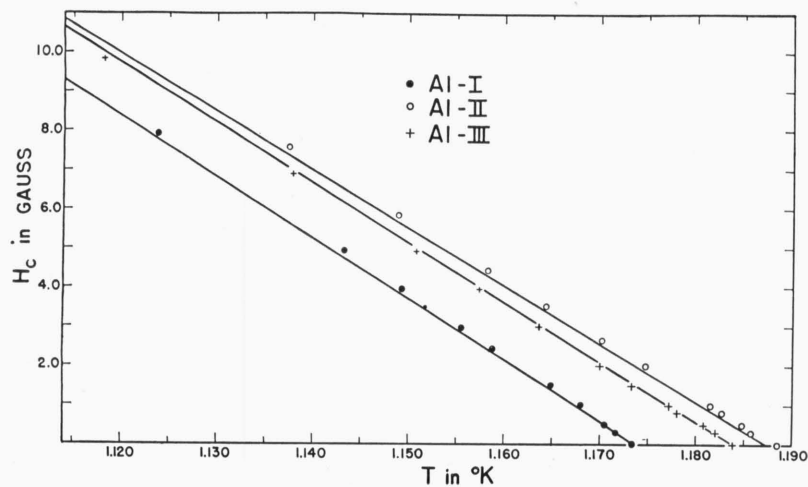


Fig. 6. The critical field curves for the three samples. Experimental points derived from the curves x versus T . Solid lines obtained from equation (6).

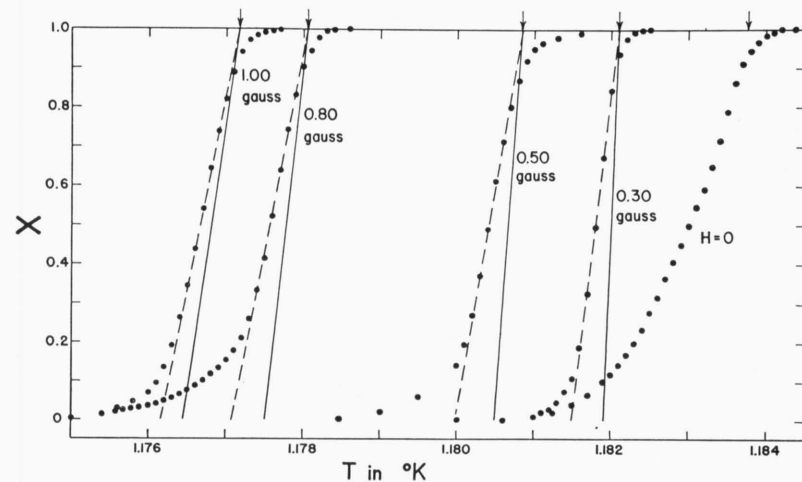


Fig. 4

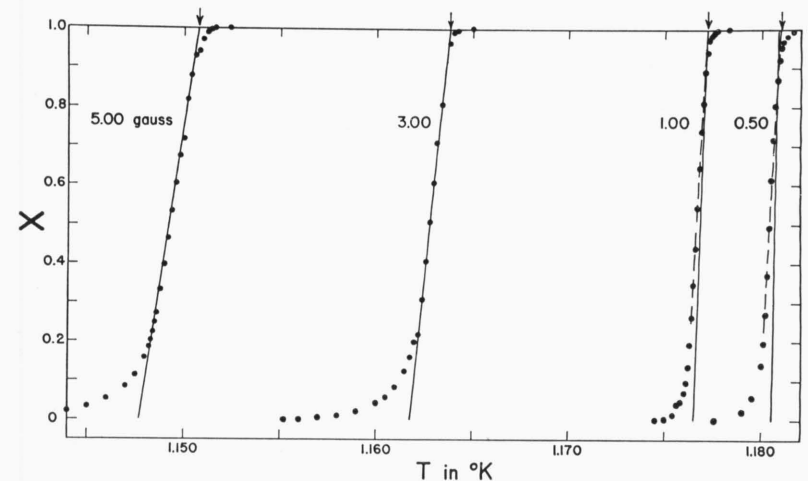


Fig. 5

Fig. 4 and 5. The concentration of the normal phase in Al III as a function of T for different fields. The solid lines are those calculated for an ideal transition in an ellipsoid with a demagnetization factor of 0.094. The dotted lines mark the way our curves were extrapolated to $x=1$ and the arrows mark the T_c so obtained.

KEESOM and KOK for Thallium²¹ and is shown in Fig. 4 and 5. For $H_c = 0$ the curve is derived from eq. (1).

C) The critical curve

The temperature T_c at which the transition was complete was localized by the intersection of the straight dotted line extrapolation in Fig. 4 with the $x = 1$ line. Such a procedure for defining T_c seems logical because above T_c only a small part is going through transition and is not representative for the average of the sample. A similar argument for an isothermal transition when the permeability (or concentration x) was measured as a function of H_c has been used by COCHRAN, MAPOTHER and MOULD². The H_c versus T_c curve defined this way corresponds to that obtained for a long specimen with a very sharp transition, and is hence consistent with the usual definition of the critical curve. It extrapolates for all the samples to the end of the transition in zero field, as indicated by an arrow in Fig. 4. We define this temperature as the critical point in zero field, T_{c0} , and the values so found for the three samples are respectively 1.173, 1.183 and 1.188 °K. The absolute value of T_{c0} is known to 1×10^{-3} °K, while this value relative to T_c in magnetic fields is localized to within 10^{-4} °K. A plot of the critical curve for the three samples is given in Fig. 6 where it is compared to that calculated from the latent heat. (See below.) The slope $(dH_c/dT)_{H=0}$ from these curves is compared in Table 5 to that derived from thermodynamic relations.

Sample	$C_s - C_n$ (millijoules/ mole deg.)	$(dH_c/dT)_{H=0}$		
		1.	2.	3.
Al I	2.24	-156 ± 2	-158 ± 3	-161 ± 2
Al II	2.19	-153 ± 2	-148 ± 3	-149 ± 2
Al III	2.22	-154 ± 2	-153 ± 3	-151 ± 2

Table 5. The slope $(dH_c/dT)_{H=0}$ as obtained in different ways. 1. via RUTGERS equation from $C_s - C_n$; 2. from the latent heat via eq. (6); 3. from the x versus T curve, as in Fig. 4 and 5.

It will be noticed from Fig. 3 that when the field is increased from zero, the transition becomes appreciably sharper. This also happens for sample II, while for sample I this effect is hidden by the additional specific heat hump due to the smaller crys-

tal. At any rate, because of the transition broadness in zero field, the exact localization of T_{c0} is still open to discussion. However, provisorily we have taken it as the extrapolation from the $T_c - H_c$ curve.

Discussion of the Results

A) Transition temperature in zero field

Our work shows again that different samples of pure aluminum have different transition temperatures and somewhat different thermal and magnetic properties. This is particularly striking for sample I where two crystals grown under the same conditions have transition temperatures differing by two millidegrees. For these two crystals, (dH_c/dT) proved to be the same. So far, comparing our data with the most recent ones of other workers, there seems no clear relation between purity and transition temperature. It has been found by CHANIN, LYNTON and SERIN²² that small amounts of impurity in specimens prepared in identical ways decrease the temperature T_{c0} . Yet our purest sample, Al I, showed by far the lowest transition temperature. Recent measurements of PHILLIPS²³ on 99.999% pure aluminum gave $T_{c0} = 1.172$ and 1.178 °K for two specimens. It is probable that different ways of crystallization and strains produce these variations, and that aluminum is more sensitive to them than other soft superconductors. COCHRAN¹⁶ for example, finds T_{c0} for three samples of tin to be the same within one millidegree.

B) Transition width and shape

According to the present results, single crystals of aluminum in zero field can have transition widths τ of about 0.6 millidegree (sample I). τ was arbitrarily defined as the temperature region in which about 80% of the transformation took place. PHILLIPS²³ has recently observed a width of 0.2×10^{-3} °K. From τ one can obtain an estimate of the range of correlation ξ in aluminum. PIPPARD²⁴ has calculated on the basis of a fluctuation model the transition shape expected from resistivity data. Although such a calculation does not strictly apply to the transition as observed from calorimetric data, it is still reasonable to assume that the widths

²¹ W. H. KEESOM and J. A. KOK, *Physica* **1**, 595 [1934].

²² G. CHANIN, E. A. LYNTON and B. SERIN, *Phys. Rev.* **114**, 719 [1959].

²³ N. E. PHILLIPS (Private Communication). This author also obtained $C_s - C_n = 2.13$ millijoules/degree mole.

²⁴ A. B. PIPPARD, *Proc. Roy. Soc., Lond.* **203**, 210 [1950].

in both experiments should approximately be the same. In PIPPARD's theory, the metal is divided into small domains of volume v , each of constant temperature, but there are temperature fluctuations from one domain to another. The transition within each domain is assumed to be infinitely sharp. The characteristic width τ' for the whole sample is then found to be

$$\tau' = 2 \sqrt{\frac{2kT^2V}{C_n v}}$$

where k is the BOLTZMANN constant. Assuming v to be of the order of ξ^3 we obtain for our three samples the correlation range ξ of respectively $1.3 \times 10^4 \text{ \AA}$, $6 \times 10^3 \text{ \AA}$, and $6 \times 10^3 \text{ \AA}$ by equating τ to τ' . Considering our somewhat arbitrary determination of τ from the data, this is in reasonable agreement, especially for sample I, with the value $\xi_0 = 1.2 \times 10^4 \text{ \AA}$ deduced by FABER and PIPPARD²⁵ from penetration depth measurements for aluminum with a very long electron mean free path. While the ideal transition shape of C in a superconductor has yet to be calculated, one can guess that the shape for the large crystal in Al I approaches more nearly the ideal one than any of the other samples. No systematic study has been made to relate the widths to the residual resistivity, as was done by COCHRAN for tin¹⁶.

When a magnetic field is applied, the temperature span of the intermediate region depends on two different factors: the effect of the fluctuations giving a characteristic width τ' and the geometry effect of the sample which gives a width

$$\Delta T \cong n H_c \left(\frac{dT}{dH_c} \right), \quad (2)$$

where n may be an effective demagnetization factor, different from the calculated one⁸. The observed width is roughly the sum of these two contributions. If $\tau' = 0$, the expected specific heat in a magnetic field is that calculated by PEIERLS²⁶, rising sharply from C_s when the transition begins and falling abruptly to C_n when it is completed. The concentration x of the normal phase then varies linearly as a function of T with a slope given by $1/\Delta T$. In practice, while PEIERLS' calculations are qualitatively confirmed, the transitions do not start or stop as abruptly. For a cylindrical specimen in particular, one expects the transition to start gradually at a

lower temperature than for an ellipsoid; because the magnetic field is strongest at the corners, these will be first to go over into the normal state. Hence one expects a "tail" of the specific heat at the low temperature end. However the completion of the transition should be rather sharp and should not be affected by the departure from ellipticity of the sample. On the other hand the transition end may be affected by fluctuations that decrease its sharpness. In Figs. 4 and 5 the concentration x versus T in sample III is compared to an ideal transition with the demagnetization factor $n = 0.094$ calculated for the sample. It is seen that the width due to fluctuations is drastically decreased as soon as a field is applied. At low fields, the total width is still larger than for an ideal transition, but eventually it becomes smaller. This is in agreement with the results of MAPOTHER and co-workers^{2, 8} on ellipsoids and also with recent experiments of HOPKINS and MAPOTHER¹⁹ on a sphere.

A plot of the transition width as a function of field for two samples is given in Fig. 8. The sharp decrease of the width when a small field is applied can be explained qualitatively by the argument that fluctuations are less probable in a magnetic field, this is when a latent heat is involved. Dr. FABER*, however, feels that the large widths in zero field as plotted in Fig. 8 cannot all be due to fluctuations, but rather to inhomogeneities in the samples.

C) Thermodynamic relations

For a reversible transition from a superconductive to the normal state in an applied field H_c one has the following relation for the difference in entropies¹⁰:

$$S_s - S_n = \frac{V}{4\pi} H_c \left(\frac{dH_c}{dT} \right) \quad (3)$$

regardless of the shape of the specimen. The latent heat for a transition that is sharp enough will be given to a good approximation by

$$L = - \frac{V T_c}{4\pi} H_c \left(\frac{dH_c}{dT} \right). \quad (4)$$

From equation (3) one obtains by differentiation $C_s - C_n$, which in zero field becomes RUTGERS equation

$$C_s - C_n = \frac{V T_c}{4\pi} \left(\frac{dH_c}{dT} \right)^2. \quad (5)$$

²⁵ T. E. FABER and A. B. PIPPARD, Proc. Roy. Soc., Lond. A **231**, 336 [1955].

²⁶ R. PEIERLS, Proc. Roy. Soc., Lond. A **155**, 613 [1936].

* T. E. FABER, Private communication.

To deduce the critical field curve from the latent heat results we have integrated equation (4) graphically:

$$H_c^2 = \frac{8\pi}{V} \int_{T_c}^{T_{co}} \frac{L}{T} dT. \quad (6)$$

The curve so obtained has been compared in Fig. 6 with that deduced experimentally. The slope $(dH_c/dT)_{H=0}$ has been calculated from latent heat data by taking the limit of $4\pi L/VT H_c$ when H_c tends to zero. The molar volume $V = 9.87 \text{ cm}^3$ was taken from X-ray data of FIGGINS, JONES and RILEY²⁷. These two calculated sets of $(dH_c/dT)_{H=0}$ values are compared to the experimental ones in Table 5. One notices that for sample Al III the consistency of the thermodynamic relations is satisfied within the experimental error. For Al II, the calculated critical curve is not quite parallel to the experimental one and shifted by about 10^{-3}°K . Hence a somewhat lower value of T_{co} is reached than that found by extrapolating the experimental critical curve. This is shown in greater detail in Fig. 7. The same be-

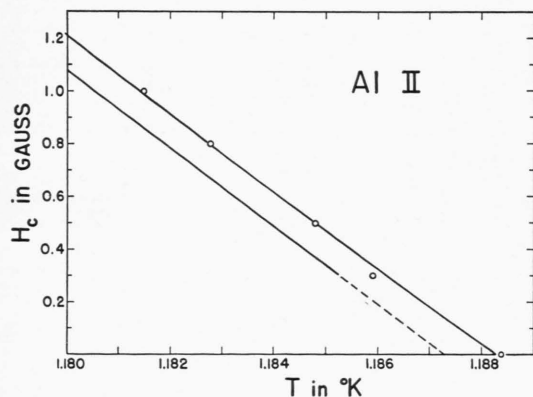


Fig. 7. The critical curve of Al II for small fields. Upper line and experimental points; derived from the x versus T curves. Lower line: calculated from latent heats via eq. (6). For $H=0$ it extrapolates to about 1.187°K , while it should extrapolate to 1.188°K . Curving the dotted portion toward 1.188°K would change $(dH_c/dT)_{H=0}$ and RUTGERS' equations would not be satisfied.

havior was recently found by HOPKINS and MAPOTHER¹⁹, who observed a difference in T_{co} of two millidegrees. It may be noted here that the transition shape they found in zero field was almost identical so that for sample II. For Al I, while there is no

such shift in T_{co} , one also finds a somewhat different critical curve, although the discrepancy is almost within experimental error. One might try to explain these discrepancies in two ways: 1) possible flux trapping in the specimen when it was

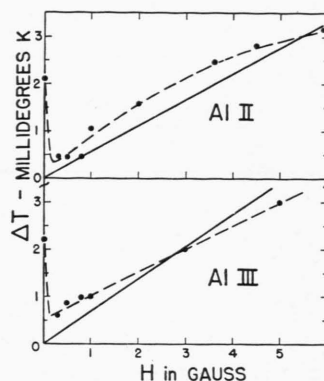


Fig. 8. The transition width for Al II and Al III as a function of the applied magnetic field below 5 gauss. The solid line is calculated from equation (2). The sharp decrease of the transition width when a field is applied is apparent. For sample I, the width is not so clearly defined because of the double transition and is not reproduced here.

cooled through the transition. This explanation seems unlikely because care was always taken to cool the specimen through the transition in zero field. 2) The experimentally obtained critical curve is incorrect because the temperature T_c may not necessarily be located where we have defined it. To satisfy even better the thermodynamic relations for Al I, T_c would be approximately located at $x = 1/2$ for the curves similar to the ones shown in Figs. 4 and 5, this is in the intermediate state. To be consistent, however, one would also have to take a different value of the magnetic field from that applied externally, due to the geometry of the sample. Near $x = 1/2$, the average field acting on the superconductive domains would be about $H_c(1 - n/2)^{-1}$, although it is difficult to calculate exactly the field distribution throughout the sample. The net effect of decreasing T_c and increasing H_c would be to bring the experimental points toward the curve we have already obtained. We cannot explain these small discrepancies between the experimental and the calculated critical curve in terms of a reversible transition. It is possible that some irreversibility may have taken place regularly during the transitions in these two samples. It is interesting to note that our results for Al I are similar to the findings of

²⁷ B. F. FIGGINS, G. O. JONES and D. P. RILEY, *Phil. Mag.* **1**, 747 [1956].

COCHRAN for single crystals of Ta and Sn although the effect observed here is much smaller. He also found that the experimental critical curve was steeper than that derived from the latent heat. The values of $(dH/dT)_{H=0}$ obtained for our three samples are lower than those obtained from magnetization data on a long sample⁸. An attempt to explain this has been made by HOPKINS and MAPOTHER¹⁹.

Conclusions

1) For all the specimens investigated, we have found that the thermodynamic properties are consistent with a reversible superconductive transition although there are small discrepancies which fall almost within the experimental error. It is possible that some small irreversible effects may take place, although the situation is not clear and requires some more experiments.

2) The sharpness of the transition in zero field is of the order expected from PIPPARD's fluctuation theory, but the transition shape and T_{c0} vary from sample to sample, perhaps due to different strains. The width due to fluctuation decreases markedly when a field is applied. We hope to study this effect further.

3) A λ -type anomaly at the transition in zero field could not be detected in aluminum in agreement with measurements on other superconductors. Hence the superconductive transition in zero field still seems the best example of a second order transition.

A study of the consistency between the thermodynamic quantities for some other superconductors, especially the hard ones, seems interesting. We have therefore started measuring the properties of a single crystal of molybdenum near its transition point, $\sim 0.95^\circ\text{K}$ ²⁸.

Acknowledgments

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²⁸ T. H. GEBALLE, B. T. MATTHIAS, E. CORENZWIT and G. W. HULL, Jr., Phys. Rev. Letters **8**, 313 [1962].