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**Author**

Phillips, Norman E.

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Norman E. Phillips

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## HEAT CAPACITY OF SUPERCONDUCTING ZINC

Norman E. Phillips

Department of Chemistry and Radiation Laboratory,  
University of California,  
Berkeley, California

Zinc provides an interesting example for the study of the electronic heat capacity of superconductors because it shows the sharp transition characteristic of the ideal superconducting state and at the same time the lattice heat capacity is relatively small, amounting to only 3% of the total at temperatures just below the transition temperature. This report describes the results of measurements on superconducting and normal zinc between  $0.15^{\circ}$  and  $1.1^{\circ}\text{K}$ .

Temperatures below  $1^{\circ}\text{K}$  were obtained by the adiabatic demagnetization of copper potassium sulfate. This salt was chosen in the belief that its susceptibility follows a Curie-Weiss law to  $0.1^{\circ}\text{K}^{-1}$ .<sup>1,2</sup> The zinc sample was connected to the salt pill through a superconducting heat switch and a mechanical heat switch was used to provide thermal contact between the salt and a helium vapor pressure bulb. A carbon resistance thermometer attached to the sample was calibrated against the mutual inductance of a set of coils surrounding the salt pill and the mutual inductance,  $M$ , was in turn calibrated against

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1 C.G.B. Garrett, Ceremonies Langevin-Perrin, Paris, 1948.

2 N. E. Phillips, Phys. Rev. 100, 1719 (1955).

the temperature,  $T$ , calculated on the Leiden 1955 scale. Temperatures below  $1^{\circ}\text{K}$  were calculated from the relation

$$N = A + B/(T - \Delta) \quad (1)$$

in which the constants  $A$ ,  $B$ , and  $\Delta$  were determined by plotting  $N$  vs  $(T - \Delta)^{-1}$  for temperatures between  $1.1^{\circ}$  and  $4.2^{\circ}\text{K}$  and for various values of  $\Delta$ . The best straight line fit was obtained for  $\Delta = 0.033^{\circ}$  and this value was used in the calculations. A more detailed account of the experimental method has been given in connection with measurements on copper and aluminum.<sup>3</sup>

The sample used was a single crystal of 99.999% zinc grown in a helium atmosphere and showing a sharp superconducting transition. A heating curve taken through the transition region at a constant rate of heat input changed slope by a factor of  $2.3 \pm 0.1$  within a temperature interval of  $0.001^{\circ}$  at  $0.825^{\circ}\text{K}$ . The discontinuity in heat capacity estimated by extrapolation of measured heat capacity points to  $0.825^{\circ}$  was by a factor of 2.2.

Figure 1 shows that for temperatures above  $0.5^{\circ}\text{K}$  the normal state heat capacity,  $C_n$ , is given by

$$C_n = \gamma T + \beta T^3 \quad (2)$$

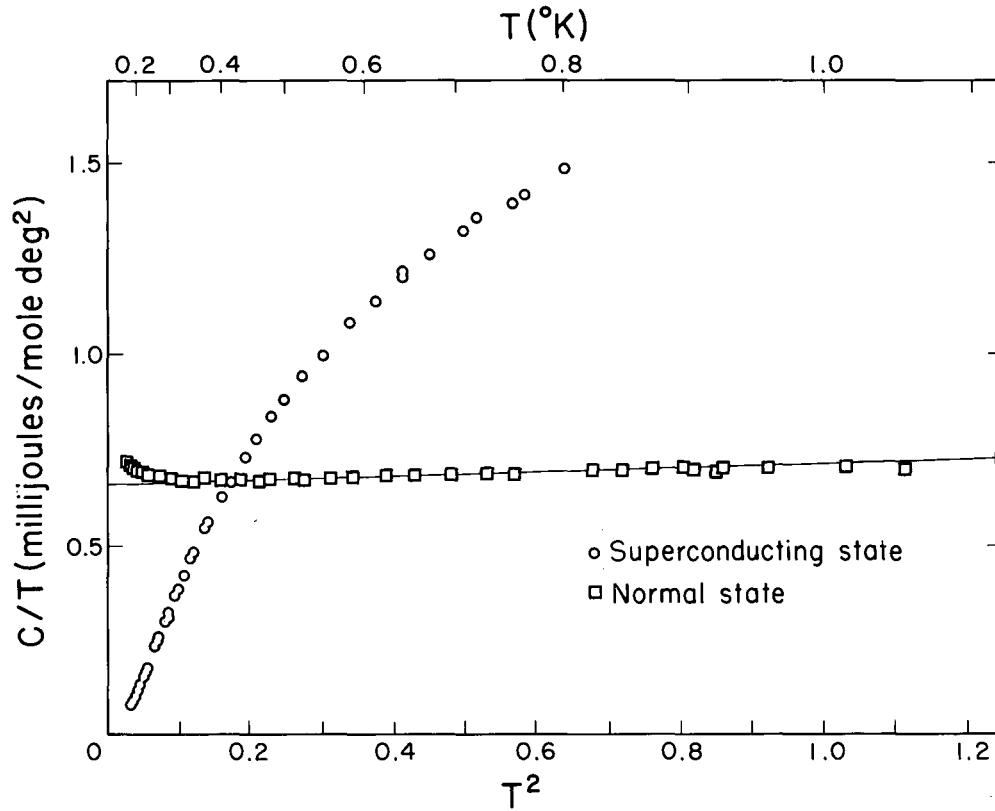
to within the experimental precision of about 1%. The value of  $\gamma$  obtained from the straight line in the figure is 0.66 millijoules/mole deg.<sup>2</sup> The lattice heat capacity at these temperatures is too

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<sup>3</sup>N. B. Phillips, Proceedings of the Fifth International Conference on Low Temperature Physics, Madison, Wisconsin, August, 1957. The University of Wisconsin Press, 1958.

Figure 1

Heat capacity of zinc in the normal and superconducting states.



small to permit an accurate estimate of  $\beta$ . Below  $0.3^{\circ}\text{K}$   $C_n$  is greater than  $\gamma T + \alpha T^3$ , the difference amounting to 5% at the lowest temperatures. This apparent anomaly in the heat capacity is very probably due to errors in the calibration of the thermometer. For example, if  $\Delta$  is taken as  $0.023^{\circ}$  instead of  $0.033^{\circ}$  and the values of  $A$  and  $B$  are changed in such a way as to preserve the fit of Eq. (1) at  $1.5^{\circ}$  and  $4.0^{\circ}\text{K}$ , the normal state points in Figure 1 all fall on a straight line parallel to that shown in the figure but with a value of  $\gamma$  about 1% smaller. With these values of  $A$ ,  $B$  and  $\Delta$  Eq. (1) would not fit the calibration points as well but the difference would amount to at most  $0.003^{\circ}$  and is not large compared to the uncertainties involved in the measurement of helium vapor pressures and in the vapor pressure-temperature relation itself. It must be concluded that within the accuracy of the experiment the normal state heat capacity is adequately represented by Eq. (2). Within the combined experimental errors this is in agreement with an extrapolation of calorimetric measurements from above  $1^{\circ}\text{K}$ .<sup>4</sup>

The electronic heat capacity in the superconducting state,  $C_{es}$ , has been obtained by subtracting the lattice heat capacity from the total in the usual way and is shown in Figure 2 as a plot of  $\log(C_{es}/\gamma T_c)$  vs  $T_c/T$ , where  $T_c$  is the zero field transition temperature,  $0.825^{\circ}\text{K}$ . An equation of the form

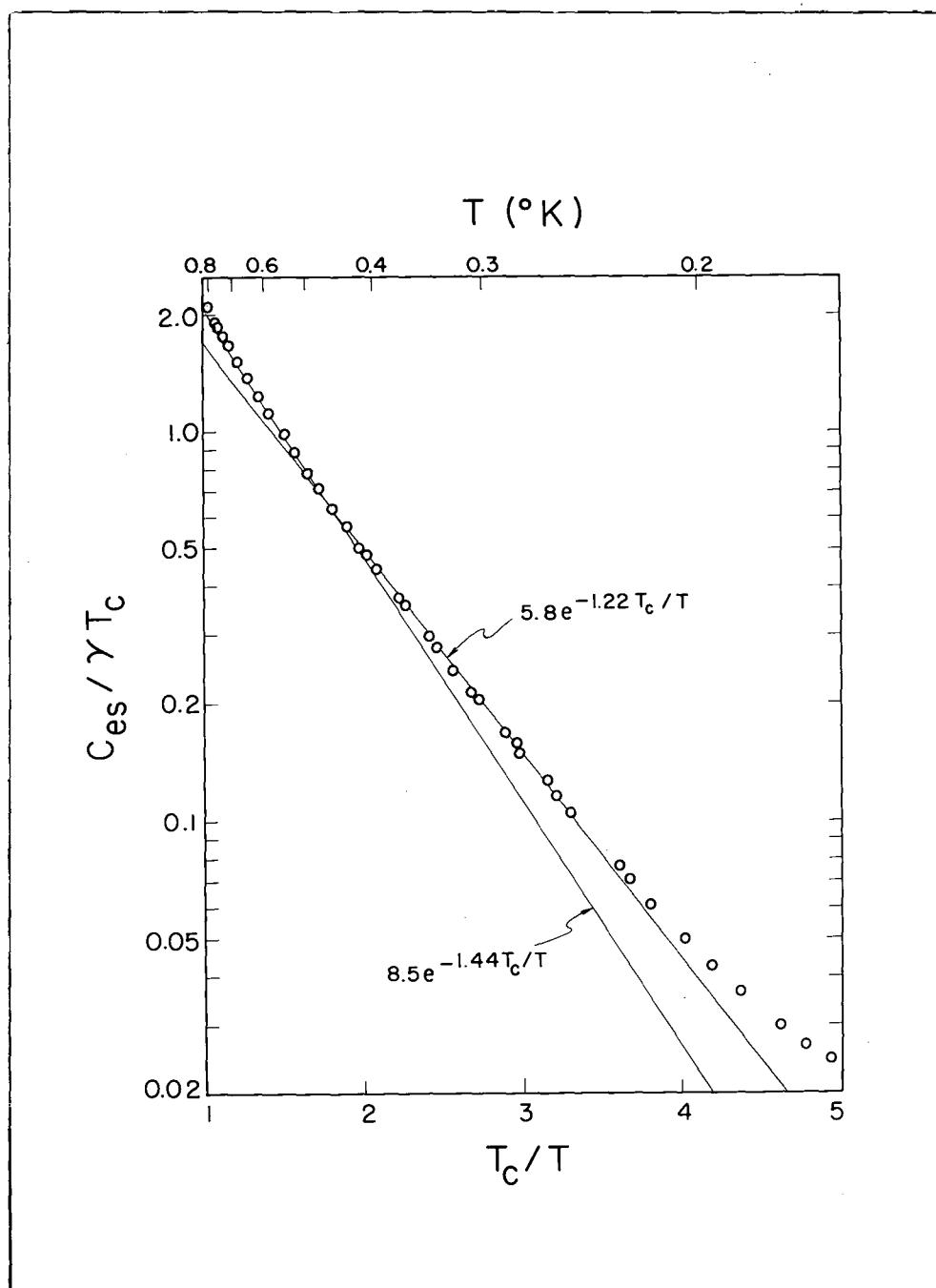
$$C_{es}/\gamma T_c = a e^{-b T_c/T} \quad (3)$$

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<sup>4</sup> A. A. Silvildi and J. G. Daunt, Phys. Rev. 77, 125 (1950).

Figure 2

Electronic heat capacity in the superconducting state.



has been shown to fit experimental data for vanadium,<sup>5</sup> tin,<sup>6</sup> and aluminum<sup>3</sup> for temperatures from  $T_c/T = 1.5$  to about  $T_c/T = 3.5$  and is also given by the theory of Bardeen, Cooper and Schrieffer<sup>7</sup> in this same range of reduced temperatures. It is apparent that Eq. (3) is not adequate to represent the present data but several straight lines are included in Figure 2 for the purpose of providing a comparison with other superconductors and with the theory. The values of  $a$  and  $b$  determined by the experimental points between  $T_c/T = 2$  and  $T_c/T = 3$  are 5.8 and 1.22 respectively. When these values are compared with 9.17 and 1.5 for vanadium<sup>5</sup> and tin,<sup>6</sup> and 7.6 and 1.32 for aluminum,<sup>3</sup> all at the same reduced temperatures, it is evident that the law of corresponding states of the Bardeen, Cooper and Schrieffer theory is not obeyed. The values of  $a$  and  $b$  predicted by the theory are 8.6 and 1.44.<sup>7</sup>

The lowest temperature points must be interpreted with some caution because of the uncertainty in the temperature scale, but the deviations from Eq. (3) are outside the estimated experimental error. Any error in the thermometer calibration will change the normal and superconducting state heat capacities by the same factor, and while the lowest temperature normal state points are 5% higher than expected, the corresponding superconducting state

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5 W. S. Cerak, B. B. Goodman, C. B. Satterthwaite and A. Waxler, Phys. Rev. 102, 656 (1956).

6 W. S. Cerak and C. B. Satterthwaite, Phys. Rev. 102, 662 (1956).

7 J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev. 103, 1175 (1957).

points are greater than  $5.8 \gamma T_c \exp(-1.22T_c/T)$  by 8%. A re-calculation of the superconducting state points using  $\Delta = 0.028^\circ$  as discussed above for the normal state does not appreciably alter their fit to an exponential.

The difference in heat capacity between the normal and superconducting states has been integrated to obtain the critical field  $H_c$  as a function of temperature. The value of  $H_c$ , the critical field at absolute zero, is 51.8 gauss, in good agreement with the value 52.5 gauss obtained by an extrapolation of direct magnetic measurements.<sup>8</sup> At  $T_c/2$  the critical field is about 5% less than that calculated from the parabolic temperature dependence.

The author wishes to express his appreciation to the National Research Council for a post-doctoral fellowship held at the time these experiments were undertaken.

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<sup>8</sup> B. B. Goodman and E. Mandose, Phil. Mag. 42, 594 (1951).

Figure 3

Critical field curve, shown as deviation from the parabolic temperature dependence.

