Heat Capacity of Sodium and Potassium at Temperatures below 1°K

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The heat capacities of sodium and potassium have been measured from about 0.15°K to just above 1°K. No anomaly was observed in either case: the heat capacity could be represented by the sum of a term linear in temperature and a cubic term. Values of the Debye temperatures and effective masses of the conduction electrons are given.

THE alkali metals are interesting examples for a comparison of the electronic heat capacity, γT, with theoretical predictions. The experimental situation is complicated by the low Debye temperatures of the heavier members of the series and by the existence of a martensitic transformation in lithium and sodium.[1] Roberts[2] has shown that for potassium the T^3 region of the lattice heat capacity is not reached above 1°K. In the case of sodium, Rayne[3] has observed an anomaly in the heat capacity at 0.9°K which he associated with the martensitic transformation. As part of a program to obtain the effective mass ratios of the conduction electrons in the alkali metals, we have made heat capacity measurements on sodium between 0.14° and 1.4°K and on potassium between 0.17° and 1.1°K.

Samples of 99.99% purity were cast into the calorimeters under an inert atmosphere. Temperature measurements were based on an extrapolation of the susceptibility of copper potassium sulfate according to a Curie-Weiss law. Normal state measurements on aluminum[4] and zinc[5] by the same method gave results which were in agreement with expectation above 0.3°K but which were 10% higher than expected at 0.15°K. This discrepancy was assumed to be a consequence of differences between the magnetic and thermodynamic temperatures. Figure 1 shows the total heat capacity of

sample and calorimeter. In both cases C/T deviates from linearity in T^2 by the same percentage as it did for aluminum and zinc.

Within the temperature range of the measurements, the sodium sample shows no heat effect that can be attributed to the martensitic transformation.[6] This is in accord with the x-ray measurements[1] which show that the reverse transformation does not start below 40°K. The difference between these results and those of Rayne[3] is presumably related to the sensitivity of the martensitic transformation to strains and thermal treatment. The data give values for the Debye temperature, γ, and the effective mass ratio of 156°K, 1.45×10^{-3} joules/mole deg², and 1.33, respectively. These values are, of course, averages for the cubic and hexagonal martensite phases. Their evaluation for either phase alone would require a simultaneous determination of the amounts of the two phases. This might be achieved by extending the measurements to high enough temperatures to measure the heat of the reverse transformation[7] or to low enough temperatures to observe the nuclear quadrupole heat capacity which can be expected in the hexagonal phase.[8]

In potassium there is no martensitic transformation above helium temperatures[1] and no indication of one was found in the present measurements. We find for the Debye temperature, γ, and effective mass ratio 89.9°, 2.2×10^{-3} joules/mole deg² and 1.3, respectively. In this case there is a possible error of about 5% in γ produced by an uncertainty in the heat capacity of the empty calorimeter.

Finally, we wish to point out that the similarity of the deviations from linearity of the C/T vs T^2 plot for sodium, potassium, aluminum, and zinc supports the original conclusion that the effect is produced by errors in the temperature scale and is not a property of the samples. In particular, it is improbable that the measurements on zinc show a nuclear quadrupole heat capacity as suggested by Seidel and Keesom,[9] and there is then no basis for their estimate of the quadrupole coupling constant or their reevaluation of the superconducting state parameters.
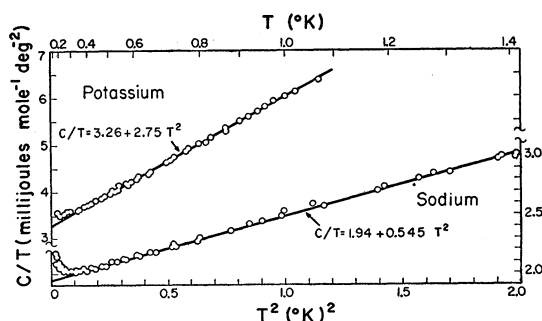

FIG. 1. C/T vs T^2. C is the heat capacity of sample plus calorimeter per mole of sample. The corrections to C/T for the calorimeters were estimated from the known heat capacities of the material used (largely copper) and are $0.49 + 0.036T^2$ and $1.02 + 0.07T^2$ millijoules/mole deg² for sodium and potassium, respectively.

[1] C. S. Barrett, Acta Cryst. **9**, 671 (1956).
[2] L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).
[3] J. Rayne, Phys. Rev. **95**, 1428 (1955).
[4] N. E. Phillips, Phys. Rev. **114**, 676 (1959).
[5] N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).

[6] Similar results above 0.4° have been obtained by R. E. Gaumer and C. V. Heer [Fourteenth Calorimetry Conference, Yale University, September, 1959 (unpublished)].
[7] D. L. Martin, Phys. Rev. Letters **1**, 4 (1958).
[8] A heat capacity contribution of this type has been observed in rhenium [P. H. Keesom and C. A. Bryant, Phys. Rev. Letters **2**, 260 (1959)], bismuth [N. E. Phillips, Phys. Rev. **118**, 644 (1960)] and in gallium [N. E. Phillips (to be published)].
[9] G. Seidel and P. H. Keesom, Phys. Rev. Letters **2**, 261 (1959).