

Specific Heat of Sodium at Low Temperatures

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Specific heat measurements in the temperature range 0.4° to 1.5°K on two samples of sodium metal are reported. A thermal cycling procedure was used to partly inhibit the martensitic transformation and thus obtain information on the properties of the two phases of sodium. It is concluded that the electronic specific heat coefficient (γ) of the bcc phase is probably slightly larger than that of the hcp phase but with 95% confidence the difference does not exceed 20%. A statistically significant variation (of unknown cause) of the apparent γ of one sample was observed. It is suggested that the wide variation in experimental γ values reported may be due to this cause rather than to the martensitic transformation.

INTRODUCTION

BARRETT¹⁻³ discovered that sodium metal undergoes a spontaneous transformation of the martensitic, or diffusionless, type on cooling below about 35°K when some of the body-centered cubic phase transforms to a faulted close-packed phase. Because of this transformation, measurements of the electronic specific heat of sodium by low-temperature calorimetry are necessarily made on a two-phase system. However measurements on various physical properties of sodium (electrical resistance,⁴ specific heat,⁵ volume change on transformation,⁶ and metallographic examination⁷) have shown that it is possible to partly inhibit the spontaneous transformation by means of a suitable thermal cycling procedure. By now there is considerable evidence^{4,7} to suggest that an unstrained, large-grained piece of sodium⁸ cooled from room temperature to liquid helium temperatures will contain roughly equal amounts of the two phases. If the sodium is now warmed to 80°K the material reverts entirely to the bcc phase, but the cold work resulting from the transformation and reversion does not anneal out and will partly inhibit the retransformation if the sodium is again cooled to liquid helium temperatures, so that now only about 25% of the sodium transforms into the low temperature phase. Thus, by making specific heat measurements on sodium cooled directly to liquid helium temperatures from room temperature, and then again after the sample has been cycled up to 80°K and back to liquid helium temperatures, it should be possible to detect if there is any difference in the electronic specific heats of the two phases.

EXPERIMENTAL

The measurements were made in a He³ cryostat using a superconducting lead wire heat switch to cool the calorimeter to the temperature of the He³ can. A

full description of the apparatus will be given elsewhere.⁹ Temperature measurement was by means of "Speer" carbon resistors which were calibrated against the vapor pressure¹⁰ of He³.

Measurements were made on two different samples of sodium. The first sample (the "cast" sample) was prepared from sodium kindly supplied by Philips, Eindhoven. This material normally has a residual electrical resistance at 4°K of about 2×10^{-4} of its ice-point resistance, indicating a very high purity. The metal was cast into a small copper calorimeter vessel carrying the carbon thermometer and heater. To facilitate the sealing operation the calorimeter was filled with argon gas at a pressure of one atmosphere. Since the use of helium exchange gas within the calorimeter was considered to be undesirable, thermal contact between the sample and the calorimeter was made solely by metallic contact and to improve this a copper wire, attached to the calorimeter, ran through the sodium. The thermal capacity of the empty calorimeter was measured on two separate occasions before filling with sodium. The weight of sodium metal (after buoyancy corrections) was 6.04 ± 0.04 g. The thermal capacity of the sodium was almost twice that of the empty calorimeter at the lowest temperatures and about four times as big at the highest temperatures.

The second sample (the "block" sample) of sodium was cut from a block of commercially pure sodium (having a residual resistivity of 6×10^{-4} which indicates rather high purity) and measured on a "tray" calorimeter,^{9,11} thermal contact being established by a film of silicone grease. The weight of the sodium metal, after buoyancy correction, was 24.606 ± 0.056 g, and the weight of oxide, etc., contamination less than 0.08 g. (Full details of the weighting procedure are given elsewhere.⁹) The thermal capacity of this sample was more than ten times that of the "empty" calorimeter.

RESULTS

Each time a sodium sample was cooled to liquid helium temperatures the carbon thermometer was cali-

¹ C. S. Barrett, *Am. Mineralogist* **33**, 749 (1948).

² C. S. Barrett, *J. Inst. Metals* **84**, 43 (1955).

³ C. S. Barrett, *Acta Cryst.* **9**, 671 (1956).

⁴ J. S. Dugdale and D. Gagan, *Proc. Roy. Soc. (London)* **A254**, 184 (1960).

⁵ D. L. Martin, *Proc. Roy. Soc. (London)* **A254**, 433 (1960).

⁶ Z. S. Basinski and L. Verdini, *Phil. Mag.* **4**, 1311 (1959).

⁷ D. Hull, and H. M. Rosenberg, *Cryogenics* **1**, 27 (1960).

⁸ A piece of sodium annealed at room temperature and with no dimension less than a few mm satisfies these requirements.

⁹ D. L. Martin, *Proc. Roy. Soc. (London)* (to be published).

¹⁰ S. G. Sydorak and T. R. Roberts, *Phys. Rev.* **106**, 175 (1957).

¹¹ D. L. Martin, *Phil. Mag.* **46**, 751 (1955).

TABLE I. Summary of results on the two samples of sodium, and check-results on copper.

No. of days from start of experiment	Sample ^a	Thermal history ^b	θ (°K) ^c	γ ($\mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$) ^c
1	Copper	...	320_{-20}^{+27}	161 ± 3
24	Na calorimeter filled	380°K		
28	Cast Na	0.4°K 290°K	No measurements	Poor operation of thermal switch
30	Cast Na	4.2°K 290°K	No measurements	Broken wire
31	Cast Na ¹	0.4°K 80°K	154 ± 6	370 ± 17
32	Cast Na ²	0.4°K 290°K	159 ± 4	386 ± 10
35	Cast Na ¹	0.4°K 80°K	160 ± 5	360 ± 10
36	Cast Na ²	0.4°K 290°K	154 ± 4	360 ± 11
		Cast sample left in cryostat under vacuum		
72	Cast Na ¹	0.4°K 80°K	165 ± 4	338 ± 7
73	Cast Na ²	0.4°K 290°K	158 ± 3	330 ± 8
		Cast sample removed from cryostat		
107	Cast Na ¹	0.4°K 80°K	157 ± 3	325 ± 7
108	Cast Na ²	0.4°K 290°K	157 ± 4	333 ± 10
		Cast sample removed from cryostat and remelted		
141	Copper	...	336_{-55}^{+61}	165 ± 4.5
148	Cast Na ¹	0.4°K 290°K	157 ± 6	342 ± 13
160		for a few hours		
161	Cast Na ¹	0.4°K 290°K	150 ± 5	328 ± 12
		Cast sample removed from cryostat		
224	Block Na ¹	290°K 0.4°K 80°K	155 ± 4	329 ± 10
226	Block Na ²	0.4°K 290°K	154 ± 5	338 ± 12
239	Block Na ¹	0.4°K 80°K	155 ± 4.5	323 ± 12
240	Block Na ²	0.4°K	152 ± 4	339 ± 11
268		Cast sample remelted a.m., cooled to 80°K p.m.		
269	Cast Na ¹	0.4°K	157 ± 5	342 ± 15

^a For Na¹, it is probable that about 50% of the sodium is in the hcp phase. For Na², it is probable that about 25% of the sodium is in the hcp phase.
^b This column shows the extremes of temperature to which the samples were subjected.
^c All error limits are 95% confidence limits.

brated and between 30 and 50 individual specific heat determinations were made in the temperature range 0.4° to 1.5°K. Values of the electronic specific heat coefficient γ and the Debye temperature θ were obtained from each such set of measurements by assuming that the results could be represented by the equation

$$C = (12\pi^4 R/5)(T/\theta)^3 + \gamma T,$$

where C is the specific heat and R the gas constant. This equation was fitted to the results by means of a least squares analysis from which the 95% confidence limits for the results was also obtained. The results obtained from fifteen sets of measurements on sodium are given in Table I together with the thermal history

of the samples. Three typical sets of measurements are shown in Fig. 1.

By comparing the results for copper given in Table I with the mean of values obtained by other workers⁹ ($\theta = 344 \pm 1^\circ\text{K}$, $\gamma = 164 \pm 1 \mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$), it may be inferred that the results obtained with the present apparatus are free from any significant systematic errors. However, owing to the very low thermal capacities of calorimeters and samples in this temperature region, the results for γ and θ (Table I) are subject to random errors of about $\pm 3\%$. Since Table I lists the results of fifteen separate determinations of γ and θ it is possible, to use suitable statistical procedures in order to assess the accuracy of final results and conclusions. In particu-

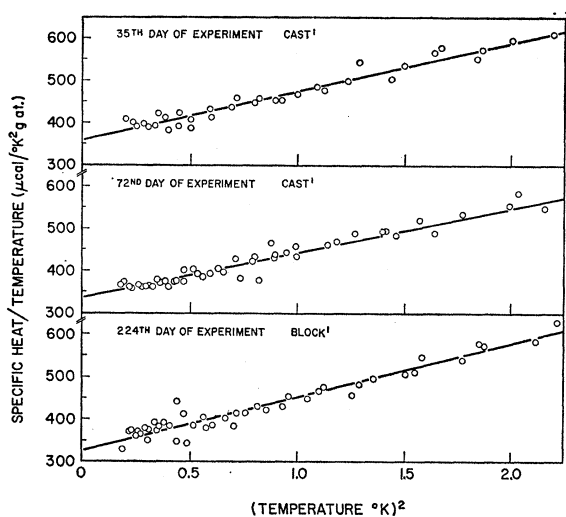


FIG. 1. The results of three typical sets of measurement on the specific heat of sodium.

lar, the technique of t tests developed by "Student"¹² for testing for significant differences between small samples has been used.

DISCUSSION

The discussion of results will be divided into three parts. First, attention will be drawn to an observed variation in the apparent electronic specific heat coefficient of the cast sample which was probably not due to the martensitic transformation. Secondly, the effect of the thermal cycling procedure will be analyzed and conclusions drawn as to the possible difference in the electronic specific heat coefficients of the two phases of sodium. Finally, the results reported here will be compared with those of other workers.

Variation of the Value of γ for the Cast Sample

Reference to Table I will show that the first four sets of measurements on the cast sample gave results for γ which are higher than those of later measurements. The results of these later measurements are in good agreement with the measurements on the block sample. It will be noticed that the variation in the γ value is not accompanied by any similar variation in the θ value. The significance of the variation in γ may be assessed by applying the t test to the difference in the means of the γ values obtained from the first-four and second-four sets of measurements, respectively. It is found that there is considerably less than one chance in a hundred that random samples from a single population would show the observed difference and hence the variation in γ must be considered as statistically significant. The variation probably represents a real change in the physi-

cal condition of the sodium within the calorimeter. [The other possibilities are as follows, and may be dismissed for the reasons stated.

(i) Experimental errors in either the earlier or later sets of measurements. This is unlikely since measurements on pure copper made before and after the variation in the γ of sodium had been observed (see Table I) showed no such variation.

(ii) Something fell off the calorimeter between the first four and later sets of measurements. But there was no significant alteration in calorimeter weight during the measurements.

(iii) There was some chemical change within the calorimeter. At the conclusion of the experiment the calorimeter was opened and, apart from a very thin grey film on the surface, the sodium looked to be very clean. Also, as mentioned above, there was no significant change in the weight of the calorimeter during the experiments. Apart from oxidation, which would have resulted in change of appearance and weight, it is difficult to see what chemical changes could have occurred.]

Efforts were made to reproduce the high γ values (see Table I) by (a) remelting the sample and measuring after annealing for about a month at room temperature, (b) measuring the sample after an anneal of only a few hours at 290°K following a previous cooling to 0.4°K, and (c) remelting the sample and cooling down as soon as possible afterwards (a few hours). No significant increase in γ was produced by these experiments.

The observed variation in γ is unlikely to be due to a variation in the amount of the low-temperature phase produced by the martensitic transformation since, on the basis of the results of the thermal cycling experiments (see later), it would correspond to a very large alteration in the amount of low-temperature phase produced. Variations of this magnitude have not been observed in previous studies on sodium.^{4,5} The high γ values were observed shortly after filling the calorimeter and the change in γ occurred during a five week period when no measurements were made, suggesting that it might have been the result of some annealing process. The rather large spread in reported γ values for sodium (Table II) might be due to this effect.

Effect of the Martensitic Transformation on γ

The results of the thermal cycling experiments will now be discussed. (The basis of the thermal cycling procedure was outlined in the introduction). By applying "Student's" t test to the differences observed in γ as a result of partly inhibiting the transformation, the effects of the variation in γ , discussed above, may be eliminated. Table I shows that six pairs of results are available for testing. The results of the test show that the samples in which the transformation is partly inhibited have a γ value which is higher by about 7 $\mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$, and the chance that pairs of samples

¹² See for example W. L. Gore, *Statistical Methods for Chemical Experimentation* (Interscience Publishers, Inc., New York, 1952). ("Student" was the nom de plume of W. S. Gosset.)

selected at random from a single population would show this difference is one in six. The 95% confidence limits for this change are $\pm 10 \mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$ Since these figures refer to a change of about 25% in the composition of the sample, it follows that the difference in γ between the hcp and bcc phases is about $30 \pm 40 \mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$ Thus the results show that the bcc phase may have a slightly higher γ value than the hcp phase but with 95% confidence the difference would not exceed 20% of γ . Making a similar *t* test on the differences of pairs of θ values it is found that the hcp phase has the higher θ by about 9°K , with 95% confidence limits of $\pm 18^\circ\text{K}$ and the chance that pairs of samples selected at random from a single population would show this difference is one in three. Thus the difference cannot be regarded as significant. It is interesting to note, however, that previously⁵ a difference of 7°K between the θ 's of the two phases at 20°K has been deduced. (The reason for the high uncertainty in the θ results is due to the smallness of the lattice contribution to the specific heat in the temperature range of measurements—about 50% of the total at 1.5°K and only 5% at 0.5°K .)

Comparison with Other Workers' Results

For comparison with the results of other workers, only the results obtained from samples with an uninhibited transformation will be considered. Furthermore, the results of the first four sets of measurements on the cast sample (with high γ values) will be ignored. The results are given in Table II. It will be seen that the results for θ are all within $\pm 1\%$. With the exception of Parkinson and Quarrington's result the γ values are within $\pm 5\%$. Parkinson and Quarrington's γ value is some 20 or 30% above the average while the high values of γ obtained initially for the cast sample in the present work are about 10% above the average. (The earlier results of Pickard and Simon¹³ and Rayne¹⁴ have been ignored in this summary since, in both cases, anomalies in the specific heat of sodium were reported which have not been confirmed by later work.)

Stern¹⁵ has recently analyzed the available experimental results for the γ of sodium and has come to the conclusion that the γ values for the bcc and hcp phases of sodium differ by some 50%. His analysis rests on the assumption that the amount of sodium transforming

¹³ G. L. Pickard and F. E. Simon, Proc. Phys. Soc. **61**, 1 (1948).

¹⁴ J. Rayne, Phys. Rev. **95**, 1428 (1954).

¹⁵ E. A. Stern, Phys. Rev. **121**, 397 (1961).

TABLE II. Comparative values of θ and γ for sodium.

Author	θ ($^\circ\text{K}$)	γ ($\mu\text{cal}/^\circ\text{K}^2 \text{ g at.}$)
Parkinson and Quarrington ^a (cut block)	158	430 ± 43
Roberts ^b (cast block)	158	328 ± 10
Gaumer and Heer ^c (cast into calorimeter)	158	315
Lien and Phillips ^d (cast into calorimeter)	156	346
This work (cast sample)	157 ± 2	335 ± 5
This work (block sample)	155.5 ± 3	326 ± 8
This work (grand mean)	156.5 ± 2	330 ± 5

^a D. H. Parkinson and J. E. Quarrington, Proc. Phys. Soc. (London) **A68**, 762 (1955).

^b L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 744 (1957).

^c R. E. Gaumer and C. V. Heer, Phys. Rev. **118**, 955 (1960).

^d W. H. Lien and N. E. Phillips, Phys. Rev. **118**, 958 (1960).

to the low-temperature phase is quite variable from sample to sample whereas there is a considerable body of evidence^{4,5,7} that, in samples of the dimensions normally used in calorimeters, this is not so. He has also ignored the possibilities of sample impurity and systematic errors between the various sets of results. The results of the thermal cycling experiments, described above, show that Stern's conclusions are most improbable.

Finally, it should be mentioned that the similarity of the values of γ for the two phases of sodium, reported here, agrees with conclusions reached by Dugdale and Gagan⁴ from an analysis of the results of their electrical resistance measurements on sodium.

CONCLUSION

The electronic specific heat coefficient of the bcc phase of sodium is probably slightly higher than that of the hcp phase. With 95% confidence the difference does not exceed 20% of γ . An unexplained variation in the γ of one sample was observed, but it must be emphasized that this does not in any way alter the conclusions relating to the martensitic transformation.

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