

using the distribution function (A1). The thermodynamic potential of the noninteracting system is then

$$\Omega^{(0)} = \frac{4}{5}N(0)V\mu_0^2 + \frac{1}{12}N(0)V\xi^2 - \mu zN - N(0)V\xi kT. \quad (\text{A7})$$

The minimum  $\Omega^{(0)}$  is at that value of  $\xi$  for which

$$\partial\Omega^{(0)}/\partial\xi = 0, \quad (\text{A8})$$

namely,

$$\xi_0 = 6kT. \quad (\text{A9})$$

The specific heat

$$C = T(\partial S/\partial T) \quad (\text{A10})$$

may be calculated from the expression (A6) obtained for the entropy. The result is

$$C_0/V = 6N(0)k^2T. \quad (\text{A11})$$

We now can see the damage done by our choice of the distribution function. The exact result for the term in the free-electron specific heat linear in temperature is<sup>12</sup>

$$C_0/V = \frac{2}{3}\pi^2 N(0)k^2T. \quad (\text{A12})$$

Thus our crude form for the distribution function re-

<sup>12</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 150.

places  $\pi^2$  by  $3^2$ . This approximation is certainly sufficient for our purposes.

We can rewrite the distribution function (A1) using (A3) and the energy variable measured relative to the Fermi energy:

$$\tilde{\epsilon} = \epsilon - \mu_0 + (1/48)(\xi^2/\mu_0) = \epsilon - \mu, \quad (\text{A13})$$

$$f(\tilde{\epsilon}) = 1: \quad -\mu_0 + (1/48)(\xi^2/\mu_0) < \tilde{\epsilon} < -\frac{1}{2}\xi,$$

$$= \frac{1}{2} - \frac{\epsilon}{\xi}: \quad -\frac{1}{2}\xi < \tilde{\epsilon} < \frac{1}{2}\xi,$$

$$= 0: \quad \frac{1}{2}\xi < \tilde{\epsilon}. \quad (\text{A14})$$

From (A9), (A13), and (A14), we may obtain the dependence of the Fermi energy on temperature for the noninteracting system

$$\mu = \mu_0 [1 - (1/48)(\xi_0^2/\mu_0^2)] = \mu_0 [1 - \frac{3}{4}(kT/\mu_0)^2]. \quad (\text{A15})$$

Once again we may compare with the exact result<sup>13</sup>

$$\mu = \mu_0 [1 - (\pi^2/12)(kT/\mu_0)^2] \quad (\text{A16})$$

and find that  $\pi^2$  has been replaced by  $3^2$ .

<sup>13</sup> F. Seitz, Ref. 12, p. 149.

## Specific Heat of Alpha-Manganese at Liquid-Helium Temperatures†

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The heat capacities of two independently prepared specimens of  $\alpha$ -Mn have been measured between 1.75 and 4.2°K. The coefficient of the contribution linear in  $T$  is found to be  $(30.6 \pm 1.5) \times 10^{-4}$  cal/mole(°K)<sup>2</sup>. This value is in reasonable agreement with that determined by Booth, Hoare, and Murphy from measurements made in the liquid-hydrogen range.

### INTRODUCTION

**P**UBLISHED reports<sup>1-6</sup> of measurements of the heat capacity of  $\alpha$ -manganese at low temperatures have

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<sup>1</sup> G. L. Booth, F. E. Hoare, and B. T. Murphy, Proc. Phys. Soc. (London) **B68**, 830 (1955).

<sup>2</sup> L. D. Armstrong and H. Grayson-Smith, Can. J. Phys. **A27**, 9 (1945).

<sup>3</sup> R. G. Elson, H. Grayson-Smith, and J. O. Wilhelm, Can. J. Res. **A18**, 83 (1940).

<sup>4</sup> N. M. Woolcott, *Proceedings of the Conference on Physics of Low Temperatures, Paris, 1955* (Centre Nationale de la Recherche Scientifique, and UNESCO, Paris, 1956), p. 286.

<sup>5</sup> C. H. Shomate, J. Chem. Phys. **13**, 326 (1945).

<sup>6</sup> K. K. Kelley, J. Am. Chem. Soc. **61**, 203 (1939).

yielded conflicting values for the electronic heat capacity and the Debye theta. It now appears that at least some of the discrepancies are attributable to the contamination of  $\alpha$ -Mn with other phases.<sup>1</sup> The present work<sup>7</sup> is a report of the helium-temperature heat capacities of two separate specimens prepared independently by different procedures and known to be in the alpha phase. The two results agree and are consistent with the heat-capacity data of Booth, Hoare, and Murphy,<sup>1</sup> obtained between 11 and 20°K using Mn specimens of known crystal structure.

<sup>7</sup> The data presented here constitute a section of the PhD thesis of G. L. Guthrie (Carnegie Institute of Technology, 1957). A preliminary report appeared in abstract form [Phys. Rev. **98**, 1181 (1955)].

We believe that it is now possible to identify, with reasonable certainty, that part of the heat capacity which varies linearly with temperature in or near the liquid-helium range.

### SPECIMEN DESCRIPTION AND EXPERIMENTAL PROCEDURES

In the present study, samples of manganese were obtained from two independent sources. The first of these (sample A) weighed 88.55 g and was in the form of granules taken from a vacuum-cast ingot<sup>8</sup> which had been annealed in argon. A spectrographic analysis of the material showed the following impurities: Al: 0.08 wt %; Si: 0.02 wt %; Fe: 0.005 wt %. A vacuum-fusion analysis showed the following gaseous impurities: H: 0.0055 wt %; N: 0.0064 wt %; O: 0.026 wt %. X-ray studies showed the sample to be in the  $\alpha$  phase.

The second sample (sample B) was in the form of electrolytic flakes.<sup>9</sup> It is part of the material from which Shull and Wilkinson prepared specimens for their  $\alpha$ -Mn neutron-diffraction studies.<sup>10</sup> These specimens were reported to be 99.98% pure, the principal impurities being Ca and Cu. Sample B weighed 34.8 g.

Magnetic susceptibility measurements on material similar to samples A and B were made by Arrott, Coles, and Goldman,<sup>11</sup> and also by Cooper.<sup>12</sup>

The heat capacities of the two specimens of  $\alpha$ -Mn have been measured between 1.75 and 4.2°K in a standard vacuum calorimeter. The apparatus and technique are described in detail elsewhere.<sup>13</sup> The samples were contained in a helium-filled metal capsule. The heat capacity of the capsule was determined in separate measurements over the same temperature range and has been subtracted from the total heat capacity. The correction amounts to approximately 4% of the measured total heat capacity for sample A and about 10% for sample B. The uncertainty in the capsule correction is included in the estimated accuracy assigned to the results given below.

The thermometer calibration followed a least-squares curve-fitting procedure.<sup>13</sup> The calibration for sample A consisted of seven points and resulted in an rms deviation of 0.0028 °K. The thermometer calibration for sample B consisted of 12 calibration points and similarly resulted in an rms deviation of less than 0.003°K. In both cases the 55E<sup>14</sup> helium vapor-pressure scale was used.

<sup>8</sup> The ingot was kindly provided by Professor J. G. Daunt of Ohio State University.

<sup>9</sup> This material was kindly provided by Professor C. G. Shull.

<sup>10</sup> C. G. Shull and M. K. Wilkinson, *Rev. Mod. Phys.* **25**, 100 (1953).

<sup>11</sup> A. Arrott, B. Coles, and J. E. Goldman, *Phys. Rev.* **98**, 1864 (1955).

<sup>12</sup> H. Cooper, thesis, Carnegie Institute of Technology, 1957 (unpublished).

<sup>13</sup> G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, *Phys. Rev.* **113**, 45 (1959).

<sup>14</sup> Available from J. R. Clement of U. S. Naval Research Laboratories.

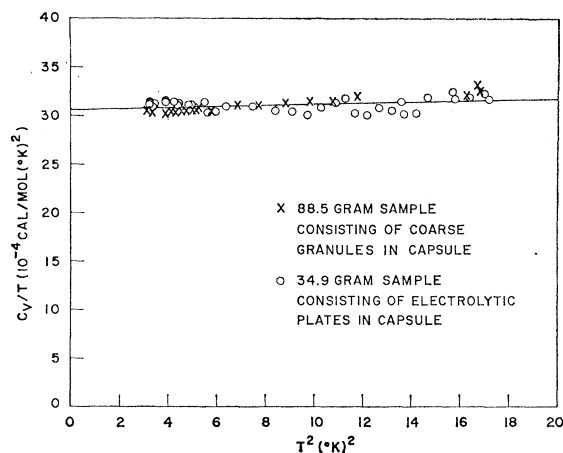


Fig. 1.  $C_v/T$  versus  $T^2$  for two independently prepared samples of  $\alpha$ -manganese. The 88.5-g sample was that supplied by Professor J. G. Daunt. The 34.9-g sample was supplied by Professor C. G. Shull. The straight line shown above goes through the center of the data of Booth, Hoare, and Murphy if the line is extended into the hydrogen range, and it fits well with their data at temperatures above 14°K.

### DISCUSSION OF RESULTS

The results are shown in Fig. 1 plotted in the form  $C_v/T$  versus  $T^2$ . From Fig. 1 we see that if the data are expressed in the usual form

$$C_p = \gamma T + (464.3/\Theta_D^3)T^3, \quad (1)$$

then the value of  $\gamma$  may be determined with reasonable accuracy, the best value for  $\gamma$  being  $(30.6 \pm 1.5) \times 10^{-4}$  cal/mole  $(^\circ\text{K})^2$ . It is found that changes in the value chosen for  $\Theta_D$  have little influence on the apparent best value for  $\gamma$ . However, owing to the extremely high value for  $\gamma$ , the reverse is not true. It is evident that scatter amounting to a few percent can almost completely obscure the  $T^3$  contribution. Therefore, in this instance, it is difficult to place confidence in a value for  $\Theta_D$  when such a value is derived solely from helium-range heat-capacity measurements.

The present value for the linear coefficient is approximately the same as  $28 \times 10^{-4}$  cal/mole  $(^\circ\text{K})^2$  reported by Booth, Hoare, and Murphy,<sup>1</sup> who used a 60-g Mn sample known to be in the  $\alpha$  phase and made measurements of the heat capacity in the hydrogen-temperature range.

It has been found possible to fit the present data and those of Booth, Hoare, and Murphy with a linear-plus-cubic relation,

$$C_p = 30.6 \times 10^{-4}T + (464.3/409)^3 T^3 \text{ cal/mole } (^\circ\text{K}). \quad (2)$$

This is the equation of the solid line in Fig. 1. Such a curve agrees well with the present helium-range data, and also agrees with the Booth, Hoare, and Murphy  $\alpha$ -Mn data at temperatures above 14°K, where their thermometer calibration might be expected to be most accurate. The data points of Booth, Hoare, and Murphy

appear to be about 5% lower than those given by Eq. (2) at temperatures below the hydrogen triple point.

The use of a linear-plus-cubic expression for the heat capacity suggests an interpretation involving a normal electronic heat capacity and a lattice heat capacity which follows a Debye law with  $\Theta_D$  constant. Such a simple interpretation may not be valid for  $\alpha$ -Mn.

Detailed calculations by Blackman,<sup>15</sup> Fine,<sup>16</sup> and Leighton<sup>17</sup> have shown that the Debye theta may not confidently be considered a constant for certain simple lattices unless  $T \leq \Theta/50$ . However, no such calculations have been made for a lattice as complicated as  $\alpha$ -Mn, which has 58 atoms per unit cell. For  $\alpha$ -Mn, at temperatures considered in this discussion, the error in  $C_p$  which would be caused by assuming a constant value for  $\Theta_D$  may be expected to be a small fraction of the total heat capacity, since the value for  $\gamma$  is found to be quite large. Once we accept the error introduced by the use of a simple Debye law with a constant value for  $\Theta_D$ , there is a negligible additional error introduced by replacing the Debye heat capacity by a term which varies as  $T^3$  for temperatures where  $T \ll \Theta/15$  ( $\sim 25$  °K). This latter substitution is, of course, not legitimate at much higher temperatures.

An additional estimate of  $\gamma$  might possibly be obtained by analyzing some data obtained at temperatures above the hydrogen range.<sup>5,6</sup> Of the available data, those of C. H. Shomate<sup>5</sup> are the most recent and perhaps the most accurate. These data extend from 52 to 298 °K. However, the heat capacity immediately below 110 °K may be expected to be complicated by a contribution from an antiferromagnetic transition whose Néel point has been observed<sup>10</sup> to be 95 °K. At temperatures above  $0.6 \Theta_D$  the  $C_p$ - $C_v$  correction for some materials has proven to be important, although it can be shown on theoretical grounds that this correction must become insignificant at sufficiently low temperatures. Consequently, in the following analysis we have rather arbitrarily limited ourselves to temperatures where the Debye contribution to the heat capacity appears to be less than 4.8 cal/mole(°K), indicating that  $T < 0.45 \Theta_D$ , and to temperatures above 110 °K so that the magnetic contribution will be of little significance.

If the heat capacity is assumed to consist of a linear term and a Debye term, it is possible to perform a relatively simple graphical analysis to determine values for  $\Theta_D$  and  $\gamma$  using data in the limited temperature range indicated above. This is done by plotting  $C_p - \gamma T$  versus  $T$  on semilog paper using several assumed values for  $\gamma$  with the log scale on the ordinate axis. A similar plot is made of  $C_p$  (Debye)<sub>calc</sub> versus  $T/\Theta$ , again using semi-

log paper. The two plots are viewed simultaneously by transmitted light with the  $T$  axes aligned. For most values of  $\gamma$  it is impossible to bring the curves into superposition. For a unique choice of  $\gamma$ , the curves may be superposed simply by relative translations along the  $T$  axis. When superposition is accomplished, the  $T/\Theta = 1$  ordinate on the Debye curve is superimposed over the value for the Debye theta for the experimental data. When such a technique is applied to C. H. Shomate's data in the temperature range from 110 to 173 °K, an excellent fit is found for  $\gamma = (25 \pm 1.5) \times 10^{-4}$  cal/mole(°K)<sup>2</sup> and  $\Theta_D \cong 376$  °K. We note moderate agreement in the values of  $\gamma$  for the three sets of data discussed, with a trend towards higher values of  $\gamma$  when the calculation is based on data at lower temperatures.

In view of the complicated and incompletely determined magnetic polarization and the large and complicated unit cell of  $\alpha$ -Mn (58 atoms on four distinct nonsimilar types of sites), we doubt that a more extended analysis of the heat-capacity curve would be fruitful. It is now believed<sup>18</sup> that magnetic moments of the various manganese atoms increase gradually with decreasing temperature at temperatures below the Néel temperature. Furthermore, the moments are unequal and not uniquely known. Under these circumstances it is not possible to calculate the expected extra entropy associated with the breakup of antiferromagnetism.

At temperatures so low that the atomic moments might be expected to be independent of temperature, the spin-wave contribution to the heat capacity<sup>19</sup> would enhance the coefficient of the  $T^3$  term, giving an apparent decrease in the Debye theta. Much more accurate data in the helium range might be expected to reveal such a situation. In the present work the data on sample A have by far the lower scatter, having benefited from a bath temperature manipulation technique<sup>20</sup> which improved the sample isolation. Sample A does, in fact, appear to exhibit a lower Debye theta than that obtained by combining the present data with those of Booth, Hoare, and Murphy.

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