

# Specific Heat of a Face-Centered-Cubic Mn-Fe Alloy at Liquid Helium Temperatures\*

CHUAN-TSENG WEI, CHIN-HUAN CHENG, AND PAUL A. BECK  
University of Illinois, Urbana, Illinois

(Received July 11, 1958)

An Fe-45 atomic percent Mn alloy, vacuum melted and homogenized at 1050°C for 48 hours, was found to consist at room temperature of a single face-centered-cubic phase, even after an excursion to liquid helium temperatures. Low-temperature specific heats were determined in the range from about 1.7 to 4.8°K. The electronic specific heat coefficient was found to be  $14.6 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>. The Debye temperature was  $\theta = 482^\circ\text{K}$ .

ELSON *et al.*<sup>1</sup> measured the electronic specific heat coefficient for  $\alpha$ -Mn at liquid hydrogen temperatures. Their value,  $\gamma = 42 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>, is the highest for any element. More recently, Guthrie, Friedberg, and Goldman<sup>2</sup> obtained the electronic specific heat coefficient for  $\alpha$ -Mn at liquid helium temperatures, and reported a value of  $\gamma = 30 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>. Even the lower one of these two values is so high that it is far outside of the scatter band that may be plotted for the electronic specific heat coefficients of the various first, second, and third long period transition elements as a function of the number of electrons outside of closed shells,<sup>3</sup> Fig. 1. It may be suspected that the anomalous value for  $\alpha$ -Mn may be a result of the complex crystal structure of this metal as compared with the other transition elements in the first, second, and third long periods. It is well known that other properties of  $\alpha$ -Mn, such as compressibility, binding energy, and vapor pressure, are also anomalous when compared with the corresponding values for other transition elements.<sup>4</sup> Recent work by Hoare and Matthews<sup>5</sup> shows that the electronic specific heat of (Cr, Fe) $\sigma$  is very much higher than that of the same alloy when transformed into the body-centered-cubic structure. The  $\sigma$  phase has a complex tetragonal structure with 30 atoms per unit cell.

If the anomalously high electronic specific heat of  $\alpha$ -Mn is a result of the complex crystal structure, it may be expected that in an alloy containing large amounts of Mn, but having a simple face-centered-cubic crystal structure, the electronic specific heat may be considerably smaller than the value that might be expected on the basis of the electronic specific heat of  $\alpha$ -Mn. Goldman and Guthrie<sup>6</sup> determined the electronic specific heat for an alloy of Fe with 11% Mn and

0.5% C, which retained the face-centered-cubic structure down to 2°K, as shown by neutron diffraction.<sup>7</sup> The result for this alloy was  $\gamma = 42 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>, a value higher even than that for  $\alpha$ -Mn itself.

In the present work, low-temperature specific heats were measured for a binary Fe alloy with 45 atomic percent Mn, which is known to retain the face-centered-cubic structure at least down to room temperature.<sup>8</sup>

## EXPERIMENTAL PROCEDURE

A 45 atomic percent Mn and 55 atomic percent Fe alloy<sup>9</sup> was melted from electrolytic Mn and Fe in an induction furnace, using a recrystallized alumina crucible and He atmosphere. The ingot was annealed at 1050°C for 48 hours in an 8% hydrogen-92% helium gas mixture and cooled to room temperature at an approximate average rate of 30°C/min. Microscopic and x-ray examination of the alloy at room temperature after the low-temperature excursions indicated that it consisted of a single phase and that it had a face-

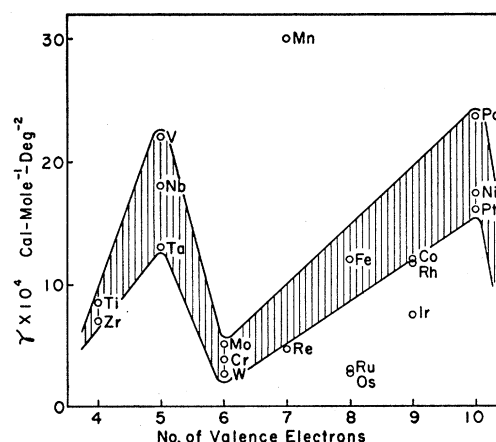


FIG. 1. Electronic specific heat of transition elements.

\* This work was supported by the U. S. Air Force, Wright Air Development Center.

<sup>1</sup> Elson, Grayson-Smith, and Wilhelm, Can. J. Research A18, 83 (1940).

<sup>2</sup> Guthrie, Friedberg and Goldman, Phys. Rev. 98, 1181 (1955).

<sup>3</sup> M. Horowitz and J. G. Daunt, Phys. Rev. 91, 1099 (1953).

<sup>4</sup> Hume-Rothery, Irving, and Williams, Proc. Roy. Soc. (London) 208, 431 (1951).

<sup>5</sup> F. E. Hoare and J. C. Matthews, Proc. Phys. Soc. (London) 71, 220 (1958).

<sup>6</sup> J. E. Goldman and G. L. Guthrie, Bull. Am. Phys. Soc. Ser. II, 1, 148 (1956).

<sup>7</sup> J. E. Goldman (private communication), based on work by L. Corliss and J. M. Hastings at Brookhaven National Laboratory.

<sup>8</sup> M. Hansen and K. Anderko, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 664.

<sup>9</sup> Chemical and spectrographic analysis: Mn, 44.58 wt %; Fe, 55.39 wt %; Al, less than 0.005 wt %; Si, less than 0.0008 wt %; O<sub>2</sub>, 0.011 wt %.

centered-cubic structure, with  $a_0=3.615$  Å. The specimen contained 1.317 moles of the alloy.

The general features of the calorimeter used are similar to those described by Corak, Garfunkel, Satterthwaite, and Wexler.<sup>10</sup> The design is shown schematically in Fig. 2. A  $\frac{1}{10}$ -watt uncoated carbon resistor of 56 ohms nominal resistance (at room temperature) was used as a thermometer, mounted in the center hole of the heater-thermometer assembly. The resistance of the thermometer as a function of the temperature was found to agree closely with the two-parameter equation

$$[(\log R)/T]^{\frac{1}{2}} = A + B \log R, \quad (1)$$

as suggested by Keesom and Pearlman,<sup>11</sup> where  $A$  and  $B$  are constants depending upon the particular carbon resistor used,  $R$  is the resistance of the thermometer in ohms, and  $T$  is the temperature in °K. The reproducibility of the thermometer constants  $A$  and  $B$  from one experiment to another was exceedingly good. The 1955 helium vapor pressure-temperature tables compiled by Clement *et al.*<sup>12</sup> was used for the calibration of the thermometer.  $A$  and  $B$  were determined by the least-squares fit of a straight line to the calibration data. Calibration of the thermometer was carried out prior to each run. The values of the constants were  $A = -1.12051$  and  $B = 0.6839$ . The resistance change in the thermometer due to temperature change in the specimen during heating was recorded automatically. The voltage drop across the thermometer, with the measuring current on, was partially balanced by an opposing emf from a K-3 potentiometer, and the difference was amplified by a model No. 9835A dc micro-volt amplifier. The output signal from the dc amplifier was recorded by a Speedomax recorder.

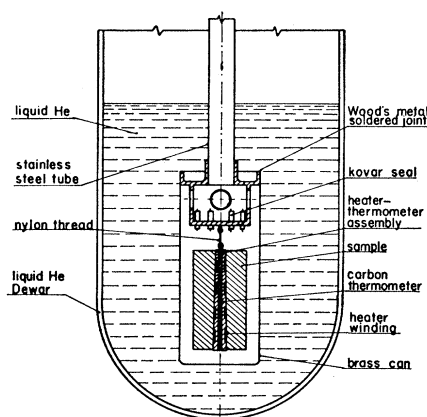


FIG. 2. Calorimeter.

<sup>10</sup> Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. 98, 1699 (1955).

<sup>11</sup> P. H. Keesom and N. Pearlman in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 297.

<sup>12</sup> Clement, Logan, and Gaffney, Phys. Rev. 100, 743 (1955), with attention directed to the "note added in proof."

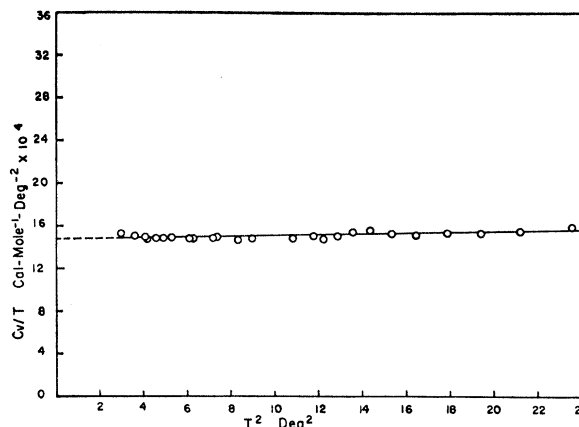


FIG. 3. Specific heat of 45 atomic % Mn-55 atomic % Fe alloy.

The over-all experimental accuracy was limited mainly by the following three factors:

(1) Pressure correction for the hydrostatic helium head in the cryostat was made by measuring the distance from the center of the cryostat can to the top of the helium bath. Uncertainty in the temperature determination, when using this correction, may have caused a maximum error of  $\pm 0.5\%$  at the  $\lambda$  point.

(2) The accuracy of the dc amplifier was  $\pm 0.4\%$ , and that of the Speedomax was  $\pm 0.3\%$ .

(3) The heat dissipated in the two short pieces of Manganin wire between the heater coil leads and the Kovar seal (introduced for heat insulation) may have amounted to  $\pm 1\%$  of the heat input. Errors in the measurement of all other quantities were negligible in comparison with these three factors. The probable over-all accuracy of the specific heat measurements was about  $\pm 2\%$ .

## RESULTS

Two successful runs were made with the same alloy specimen, and the two sets of data agreed well within the experimental accuracy. The results of the second run, which was the better one, are shown in Fig. 3. The value of the electronic specific heat coefficient was  $14.6 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>. The slope of the line in Fig. 1 corresponds to a Debye temperature of  $\theta = 482^\circ\text{K}$ .

## DISCUSSION

The value of the electronic specific heat coefficient for the Fe+45 atomic percent Mn alloy obtained in the present work is only slightly higher than the corresponding value for Fe ( $12 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup>).<sup>13</sup> Clearly, the Mn in this face-centered-cubic alloy did not contribute to the electronic specific heat coefficient in proportion to the  $\gamma$  value for  $\alpha$ -Mn. As explained in

<sup>13</sup> G. Duyckaerts, Physica 6, 401 (1939). The electronic specific heat coefficient value of  $\gamma = 12.0 \times 10^{-4}$  cal mole<sup>-1</sup> deg<sup>-2</sup> obtained in this early work was recently confirmed by the present authors, using electrolytic iron melted in vacuum.

the Introduction, the recent work by Hoare and Matthews<sup>5</sup> suggests that, for a given chemical composition, a simple crystal structure may be expected to correspond to a lower electronic specific heat coefficient than a complex one. The present results appear to support this conclusion.

The reason for the large difference between the electronic specific heat coefficients for two face-centered-cubic alloys, one consisting of Fe+11% Mn+0.5% C<sup>6</sup> and the other the Fe+45% Mn alloy used in the present work, is not very clear. According to Goldman,<sup>14</sup> it is possible that the density of state *vs* energy curve has a very irregular shape in the region concerned, and that the difference is largely due to the increased filling up of the 3*d* shell with increased Mn content. A possible

alternative explanation might be that the very high value observed for their alloy by Goldman and Guthrie<sup>6</sup> is somehow connected with the carbon content of their alloy. No definite conclusions may be drawn at the present time as to these alternative interpretations.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor Dillon E. Mapother and Mr. F. A. Otto of the Department of Physics, University of Illinois, and Dr. J. K. Hulm of the Westinghouse Research Laboratories and Dr. N. Pearlman of the Department of Physics, Purdue University for their very valuable advice regarding the design of the calorimetric equipment and of the cryostat. Dr. Yuan-Shin Chow, of the University of Illinois, has kindly worked out the program for the necessary calculations with the Illiac Digital Computer.

<sup>14</sup> J. E. Goldman (private communication).

## Magnetic Field Dependence of the Hall Effect and Magnetoresistance in Graphite Single Crystals

D. E. SOULE

*National Carbon Research Laboratories,\* Cleveland, Ohio*

(Received June 30, 1958)

The Hall coefficient and magnetoresistance in purified (99.995%) natural graphite single crystals have been measured from 25 to 25 000 gauss at 298°, 77°, and 4.2°K with the field oriented parallel to the hexagonal axis. Special care was taken in the micromanipulation and strain-free mounting of these small soft crystals. Fast minority carriers due to Fermi-surface warping were discovered by their effect on the low-field Hall coefficient behavior. The compensating effect between the majority electron and hole densities [(5–2) × 10<sup>18</sup> cm<sup>-3</sup> with  $n_e/n_h = 1.0$ –1.15 over the above temperature range] and mobilities [(1.5–130) × 10<sup>4</sup> cm<sup>2</sup>/v sec with  $\mu_e/\mu_h = 1.10$ –0.79] makes the Hall coefficient very sensitive to the temperature, impurities, and field where it even changes sign. A quadratic low-field room-temperature magnetoresistance dependence progresses at higher fields to an impurity-insensitive  $H^{1.78}$  behavior. The large magnetoresistance ratio of graphite (~10<sup>6</sup> at 4.2°K and 23 kilogauss), along with the appearance of de Haas-van Alphen type oscillations in these properties, demonstrates the small effective masses (0.03*m*<sub>0</sub>, 0.06*m*<sub>0</sub>) and long relaxation times (2.5 × 10<sup>-11</sup> sec at 4.2°K). The mobility follows a  $T^{-1.2}$  law in the lattice-scattering region  $\gtrsim 50^\circ\text{K}$ . Low-temperature results, showing carrier density differences and mobilities to be most sensitive to impurities, substantiate the relatively high purity of these crystals.

### I. INTRODUCTION

KINCHIN'S pioneering work<sup>1</sup> revealed a remarkable field dependence of the Hall effect in the semimetal graphite. The strong variation in the Hall coefficient, *R*, included a change in sign at 77°K in addition to showing a sharp minimum in the region of liquid hydrogen and below. Such a variation is partly due to the close balance of electron and hole concentrations and mobilities, producing a small *R* that is very sensitive to a slight shift of the Fermi level. Accompanying effects are caused by the very large mobilities in the basal plane of this essentially two-dimensional highly aniso-

tropic material. Its tremendous magnetoresistance<sup>1,2</sup> is consistent with the extreme anisotropy in its zero-field resistivity.<sup>3–5</sup> Verification of the small effective masses for carriers travelling in the basal plane has been substantiated by the observation of de Haas-van Alphen type galvanomagnetic oscillations by Berlincourt and Steele<sup>2</sup> which they have correlated with those found in the susceptibility.<sup>6</sup>

The graphite crystals heretofore investigated were all of a natural origin being, in general, quite impure and

<sup>2</sup> T. G. Berlincourt and M. C. Steele, *Phys. Rev.* **98**, 956 (1955).

<sup>3</sup> K. S. Krishnan and N. Ganguli, *Nature* **144**, 667 (1939).

<sup>4</sup> A. K. Dutta, *Phys. Rev.* **90**, 187 (1953).

<sup>5</sup> W. Primak and L. H. Fuchs, *Phys. Rev.* **95**, 22 (1954), and W. Primak, *Phys. Rev.* **103**, 544 (1956).

<sup>6</sup> D. Shoenberg, *Trans. Roy. Soc. (London)* **245**, 1 (1952).

\* National Carbon Company, Division of Union Carbide Corporation.

<sup>1</sup> G. H. Kinchin, *Proc. Roy. Soc. (London)* **A217**, 9 (1953).