

Specific Heat of a Magnetite Crystal at Liquid Helium Temperatures*

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The heat capacity of a large natural crystal of magnetite was measured between 1.8 and 4.2°K. The specific heat, as a function of temperature, is resolved into two parts: a T^3 term that presumably is the lattice heat, and a $T^{\frac{3}{2}}$ term that may be identified as a spin-wave contribution to the specific heat.

BLOCH'S $T^{\frac{3}{2}}$ law¹ for the temperature decrease of the magnetization of a ferromagnet has been difficult to confirm experimentally because at very low temperatures (where Bloch's analysis is most applicable), it is necessary to measure extremely small relative changes of magnetization. However, directly associated with the Bloch magnetization law, there is a specific heat² whose entire magnitude varies as $T^{\frac{3}{2}}$. The detection of this magnetic specific heat should be feasible at very low temperatures where it would be comparable in magnitude with the lattice heat whose temperature dependence is presumably cubic. Unfortunately, in ferromagnetic metals, the large electronic heat, varying only linearly with temperature, would easily mask any small $T^{\frac{3}{2}}$ term. In the case of the ferrites, however, their electrical properties suggest that the density of states at the Fermi level and, hence, the electronic heat are extremely small. Moreover, it has been demonstrated by spin-wave arguments that the ferrimagnetism of the ferrites also leads to a $T^{\frac{3}{2}}$ variation of the magnetization³ and the associated specific heat.⁴

Calorimetric measurements were made between 1.8 and 4.2°K on a large natural crystal of magnetite (44.9 g or 0.194 mole). The use of sintered ferrite specimens was prohibited by their very low thermal conductivity, while the use of ferrite powder presented serious difficulties due to desorption of helium exchange gas inside the calorimeter. A constantan wire heater and a carbon resistor thermometer were attached directly to the magnetite crystal which was suspended by nylon thread inside a vacuum tight container within the liquid helium bath. Standard low-temperature calorimetric procedure was followed except that the extremely small heat capacity of the specimen accentuated the effects of thermal lags in our system and, hence, compelled us to develop and use a new method for computing the specific heat from the temperature-time response curves.⁵

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¹ F. Bloch, *Z. Physik* **61**, 206 (1930).

² N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), pp. 236-239.

³ H. Kaplan, *Phys. Rev.* **86**, 121 (1952).

⁴ J. S. Kouvel, Technical Report 210, Cruft Laboratory, Harvard University, February 1, 1955 (unpublished).

⁵ J. S. Kouvel, *J. Appl. Phys.* (to be published).

In Fig. 1, our results are shown as a plot of $C/T^{\frac{3}{2}}$ versus $T^{\frac{3}{2}}$, where C is the total heat capacity of the specimen. The experimental points fall very close to the straight line, obtained by the method of least squares, which gives for the molar specific heat, C_m , as a function of temperature:

$$C_m = 1.315T^{\frac{3}{2}} + 0.047T^3 \text{ millijoules/}^\circ\text{K.} \quad (1)$$

The cubic term is the lattice heat and yields a Debye temperature of 660°K which agrees reasonably well with the value of 570°K deduced from Millar's data at much higher temperatures.⁶

From a spin-wave analysis of the magnetite structure,⁴ the magnetic contribution to the molar specific heat is found to be:

$$C_{\text{magnetic}} \approx 0.113R \left\{ \frac{2(2S_B - S_A)kT}{11J_{AB}S_A S_B - 2J_{AA}S_A^2 - 4J_{BB}S_B^2} \right\}^{\frac{3}{2}}, \quad (2)$$

where S_A and S_B are the average electronic spins associated with the ionic moments of the tetrahedral and octahedral sites, respectively; R is the molar gas constant. The J 's are the absolute magnitudes of the different negative exchange interactions between nearest neighboring spins,⁷ and are found to be related

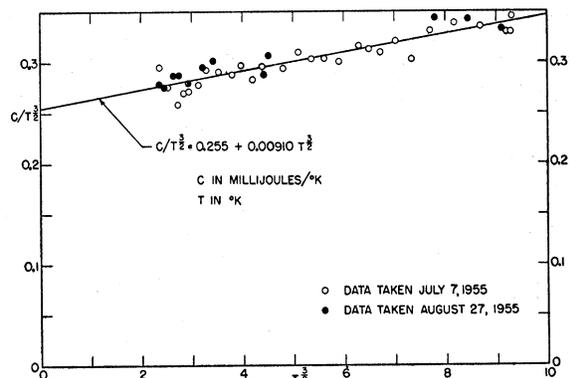


FIG. 1. $C/T^{\frac{3}{2}}$ vs $T^{\frac{3}{2}}$, where C is the total heat capacity of the magnetite crystal specimen (0.194 mole) and T is the absolute temperature.

⁶ R. W. Millar, *J. Am. Chem. Soc.* **51**, 215 (1929).

⁷ L. Néel, *Ann. phys.* **3**, 137 (1948).

to the Curie temperature, T_c , as follows⁴:

$$kT_c \simeq 4\sqrt{2}J_{AB}\sigma_A\sigma_B - (4/3)J_{AA}\sigma_A^2 - 2J_{BB}\sigma_B^2, \\ \sigma_N^2 \equiv S_N(S_N + 1). \quad (3)$$

As a first approximation, terms in J_{AA} and J_{BB} in Eqs. (2) and (3) may be considered negligible compared to terms in J_{AB} .⁷ Then, setting $S_A = 2.5$ and $S_B = 2.25$ and the $T^{\frac{3}{2}}$ term in Eq. (1) equal to the right-hand side of Eq. (2), we find that $J_{AB} \simeq 5.15k$, and from Eq. (3) that $kT_c \simeq 45.2J_{AB}$. The combination of these results gives $T_c \simeq 235^\circ\text{K}$, which is far below the directly measured value of 848°K .

It would be premature to attempt an explanation of this quantitative discrepancy in the light of only these preliminary results. We propose to extend these measurements to higher temperatures and to other ferrite crystals, and also study the effects of an external magnetic field on the spin-wave component of the specific heat.⁸

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⁸ J. S. Kouvel and H. Brooks, Technical Report 198, Cruft Laboratory, Harvard University, May 20, 1954 (unpublished).

Components of the Thermodynamic Functions of Iron

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The thermodynamic functions enthalpy, entropy, and free energy of alpha and gamma iron are determined from existing data. These functions are resolved into their magnetic, lattice, and electronic components on the basis of additivity of the respective specific heat components. The total magnetic entropy at the melting point approaches $R \ln(2s+1)$, where s is the unpaired spin per atom, indicating the validity of the method of separating specific heat components. A comparison plot of magnetic entropy *versus* temperature and saturation magnetization *versus* temperature qualitatively distinguishes the long- and short-range magnetic order. It is shown that the magnetic enthalpy at the melting point is of order kT_c , where T_c is the Curie temperature. It is further shown that in the absence of magnetic effects the γ lattice at absolute zero is more stable than the α lattice by approximately 130 cal/mole. Finally, the components of the free energy are appropriately modified for the iron-rich FeMn alloy in order to determine the phase boundaries.

INTRODUCTION

THE recent collation of Darken and Smith¹ probably contains the best values of the specific heat of α iron and the deduced specific heat of γ iron. However, the existence of antiferromagnetism in γ iron with Néel temperature $\sim 80^\circ\text{K}$ and moment ~ 0.57 Bohr magnetons,² unknown to Darken and Smith, will modify their data. Their deduced specific heat curve for γ iron which depended on equating the entropies of the two phases from 0 to 1353°K is thus altered by virtue of the magnetic entropy of γ iron and results in a more realistic Debye temperature of 335°K rather than 300°K obtained by Darken and Smith. With the established specific heat curves of both the body-centered and face-centered iron phases, the enthalpies and entropies can then be determined as a function of temperature by graphical integration with careful attention to the maintenance of consistency with the known enthalpies and entropies at the transition

temperatures, 1183°K and 1673°K . Finally, the Gibbs free-energy functions as a function of temperature can then be established from the calculated enthalpy and entropy functions according to the definition $G(T) \equiv H(T) - TS(T)$.

Since the primary objective of these calculations is the application of the thermodynamic functions to iron-rich alloys, it was necessary in our case to analyze the total free energy functions into their component parts, i.e.,

$$G(T)_{\text{total}} = G(T)_{\text{magnetic}} + G(T)_{\text{lattice}} + G(T)_{\text{electronic}}.$$

These component parts were then appropriately modified in accordance with the known properties of the alloys to reconstruct the total free-energy functions for the alloy phases. This is an extension and correction of calculations previously reported by Zener.³

COMPONENTS OF α IRON

The heat capacity data at low temperatures fit a Debye θ of 420°K . The lattice specific heat at constant pressure was then calculated from the relation

³ C. Zener, *J. Metals* 7, 619 (1955).

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¹ L. S. Darken and R. P. Smith, *Ind. & Eng. Chem.* 43, 1815 (1951).

² Susceptibility and neutron diffraction data unpublished, Corliss, Hastings, and Weiss.