The Magnetic Susceptibility of MnO as a Function of the Temperature

RAYEN WELCH TYLER, *University of Illinois*

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The magnetic susceptibility of manganous oxide for temperatures from 26 to −202°C.—There is a sharp discontinuity in the susceptibility-temperature curve at the same point, $t=-156°C$, as that in the specific heat temperature curve and a second one at a lower temperature, −188°C. The mass susceptibility at 26°C was found to be $\chi=68.6\times10^{-6}$ c.g.s. units. At −38.4°C, $\chi=73.6°\times10^{-6}$. At −154.7°C, $\chi=85.8\times10^{-6}$. At −188°C, $\chi=78.1\times10^{-6}$. At −202°C, $\chi=91.4$. The susceptibility-temperature curve follows Weiss' modification of Curie's law down to $t=-156°C$. The constants of this law were found to be $C=0.0575$ and $\theta=-548°K$. The number of Bohr magnetons in the compound calculated from experimental data is 5.7.

Introduction

The specific heat of MnO as a function of the temperature at low temperatures has been studied by R. W. Millar[1] who found that at −157°C there is a very narrow peak in the specific heat curve which rises very abruptly, from a curve gradually falling with the temperature to over thirteen times the specific heats at neighboring temperatures.

The purpose of the present investigation was to learn whether there might not be a similar discontinuity in the magnetic susceptibility curve for MnO at the temperature −157°C. This was rendered the more probable by the recent discovery by C. H. Li[2] in this laboratory of marked changes in the magnetic properties of magnetite at −160°C, where there is a discontinuity in the specific heat of that substance.

Method of Investigation

The Faraday method of measurement was used. The sample was placed at the point of maximum nonhomogeneity in the field of a large Dubois magnet with conical pole pieces. The force on it was measured with a Curie balance with an electrically controlled torsion head described by A. N. Guthrie.[3] The apparatus was calibrated by measuring the force on a sample of known susceptibility, neodymium oxide.

In the temperature range 0 to −182°C the temperatures were obtained by a copper cooling device, the ends of which were immersed in liquid air. Temperatures lower than −182°C were obtained by boiling fresh liquid air at reduced pressures. A special vacuum bottle of three chambers was designed for this purpose. The innermost chamber in which the sample swung was surrounded by a second which contained the liquid air and was evacuated through a side tube. The outer chamber was silvered and evacuated.

To prevent the condensation of oxygen upon the balance arm, the entire balance was encased in an atmosphere of hydrogen. Commercial hydrogen was used and was freed from possible traces of oxygen by passing over platinized asbestos heated to 500°C and dried by passing over ascarite and anhydrone. Temperatures were measured with a copper-constantan thermocouple. One junction was kept in ice water and the other was supported on a fine glass tube beside the balance arm at the level of the sample. The thermocouple was calibrated against the freezing points of mercury, −38.9°C, and carbon disulphide, −111.6°C and the boiling point of oxygen determined with an oxygen vapor pressure thermometer. The temperature corresponding to a given vapor pressure was computed from the equation $t=369.83/(6.98460-\log_{10}P)$.[4]

Procedure and Results

Corrections for the susceptibility of the quartz container were made in the usual way. Several

[1] Russell W. Millar, J. Am. Chem. Soc. **50**, 1875 (1928).

[2] Ching Hsien Li, Phys. Rev. **40**, 1002 (1932).

[3] Guthrie and Bourland, Phys. Rev. **37**, 303 (1931).

[4] *Tables Annuelles de Constantes et Donnees Numerique*, Vol. LVI, p. 290.

samples of MnO weighing between 20 and 30 milligrams were used. The cooling chamber was cooled to the lowest possible temperature and readings taken every few degrees as it slowly warmed up. The observed deflections, corrected for the susceptibility of the quartz container, varied from 11 to 23 cm. From the observed deflections the susceptibilities were calculated and plotted against temperature. The result was a series of curves forming a band of points whose width varied from 1 to 3 percent of the susceptibility. The graphical average of these curves is plotted in Fig. 1.

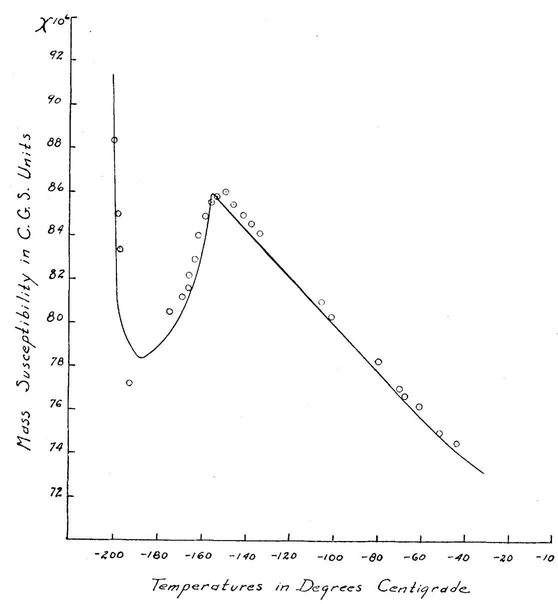

FIG. 1. Magnetic susceptibility of MnO. Average curve. Circles represent actual measurements taken in one run.

Discussion of Results

The abrupt discontinuity in the magnetic susceptibility curve at $-155°C$ is apparently to be correlated with the discontinuity in the specific heat curve, reported by Millar, at $-156°C$. The temperature difference is probably not significant because of a possible lag in the temperature of the sample behind that of the thermocouple. The susceptibility curve falls very rapidly at the discontinuity. The minimum at $-188°C$ and the subsequent steep rise at lower temperatures is without parallel in the specific heat curve.

Measurements at still lower temperatures to determine the further course of this curve should be made because the substance must either become ferromagnetic or exhibit another discontinuity. Such measurements were not possible in the present experiment without liquid hydrogen.

The susceptibility obeys the Weiss law $\chi = C/(T-\theta)$ for temperatures above $-155°C$. The Curie constant C was 0.0575 erg dynes per gauss per gram and $\theta = -548°K$. The number of Weiss magnetons was found to be 28.4. The ion Mn^{++} has the ground state $^6S_{5/2}$, a single state. The number of Bohr magnetons then is $p = g[j(j+1)]^{1/2}$, where g is the Landé splitting factor and j the total angular momentum quantum number. For Mn^{++}, $g=2$, $j=5/2$, and $p=5.92$. The ion O^{--} has a closed outer shell and is therefore diamagnetic. The number of Bohr magnetons in the compound can be calculated from experimental data by the equation $p=(1/B)(3kC/N)^{1/2}$, where B is the Bohr magneton, k, Boltzmann's constant, C, the Curie constant and N, the number of molecules per gram. From the value of C here determined, p is found to be 5.7.

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