The Magnetic Susceptibility of Manganese Pyrophosphate as a Function of Temperature

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ABSTRACT

The Magnetic Susceptibility of manganese pyrophosphate has been measured as a function of temperature from 300 to 1165°K. The Curie and Weiss constants for the substance have been found to be 4.57 and —14° respectively. The Curie constant is larger than the value predicted from theoretical considerations.

INTRODUCTION

The magnetic properties of the compounds in which manganese has a +2 oxidation state have been the subject of much experimental investigation (1). The Mn^{+2} ion normally possesses 5 unpaired electrons in the 3d subshell in a $^6S_5/_2$ state with zero net orbital moment. The Mn^{+2} ion should be strongly paramagnetic with its magnetic moment determined entirely by the unpaired electron spins. Therefore, it is not necessary to consider the degree of orbital quenching which sometimes leads to complications in the magnetic behavior of compounds of other transition metals. The negative ions or radicals, which together with manganese make up the various compounds, usually have completely paired electron systems and contribute only to the relatively weak diamagnetism which is superimposed on the paramagnetism. Furthermore, the manganous ion in its S state at moderate temperatures has an extremely small anisotropy in its magnetic behavior so that orientation effects in working with powder samples are minimized (2).

Recent investigations by the authors have been concerned with the Group VI compounds of manganese, MnO, MnS, MnSe, and MnTe (3,4,5,6). These have been found to be antiferromagnetic obeying the Weiss-Curie relationship, $\chi = C_m/T\text{-}\Theta$, where χ is the molar susceptibility, C_m the Curie constant, and Θ the Weiss constant (7). The Curie constant, C_m, can be related directly to the number of unpaired electrons. The Weiss

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constant, Θ, depends in part on the sign and magnitude of the exchange integral. The negative character of the exchange integral in antiferromagnetic substances gives rise to antiparallel coupling of spins and the characteristic temperature versus susceptibility behavior with a susceptibility maximum occurring at a rather sharply defined temperature called the Neél point. Below the Neél point the Weiss-Curie relationship is no longer obeyed.

The Group VI compounds of manganese were shown to have Curie constants somewhat lower than predicted for systems with 5 unpaired electrons. This was assumed to be due to an overlapping of unpaired orbitals among adjacent manganese ions with a resultant partial spin pairing. As the distance between closest Mn^{++} ions increased, the observed value of C_m approached the 5 electron value.

To provide further information on this effect, an investigation of other compounds with more widely separated Mn^{++} ions has been undertaken. Manganese pyrophosphate, $Mn_2P_2O_7$, is a stoichiometric compound, easily prepared in a pure state, commonly used in the gravimetric determination of manganese. It is reported to have a monoclinic structure but the lattice parameters have not been fully determined (8). From the known densities, however, the volume per Mn^{++} ion can be computed to be 64 cubic angstroms in $Mn_2P_2O_7$, compared with 24, 36, 40, and 42 cubic angstroms respectively in MnO, MnS, MnSe, and MnTe. The smaller effect of adjacent positive ions on each other in the pyrophosphate should give a value of C_m in better agreement with the theoretical one.

Some work has already been done on the susceptibility of $Mn_2P_2O_7$ (9,10,11,12). The reported results are in poor agreement, however, and extend over a limited temperature range.

EXPERIMENTAL

Measurement of Susceptibility. The method used to determine the susceptibility of $Mn_2P_2O_7$ in this study was the Faraday method. In the Faraday method a small sphere of material is suspended in a non-homogeneous field. The force on the sample is given by the expression $F = m\chi_g H\frac{dH}{dx}$, where m is the mass, χ_g the susceptibility per gram, H the field, and $\frac{dH}{dx}$ the field gradient. In the measurements taken the samples were suspended in a region in which $H\frac{dH}{dx}$ had been determined as a

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function of magnet current. The force on the sample in the field was measured with a Sartorius microbalance. The $H\frac{dH}{dx}$ values were found using samples of nickel chloride and Mohrs salt, both of which have accurately determined susceptibilities given in the literature and are commonly used as standards.

Since the Vycor capsules which contained the samples were diamagnetic, it was necessary to apply an empirically determined blank capsule correction. To permit the measurement of the susceptibility at different temperatures a Vycor tube non-inductively wound with insulated nichrome wire served as the furnace. A chromel-alumel thermocouple was placed in

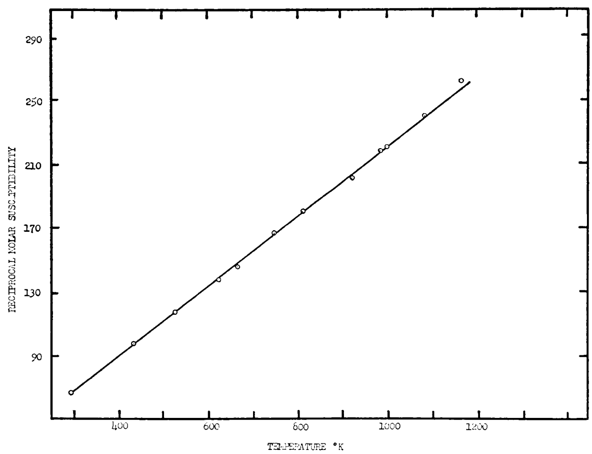

Figure 1. The Reciprocal Molar Susceptibility of Manganese Pyrophosphate as a Function of Temperature.

the lower end of the tube to measure the temperature of the samples. A brass cooling jacket was placed around the tube furnace to protect the pole pieces of the magnet at high temperatures. The entire system was evacuated and filled with helium before each run. This was done in order to remove any oxygen, which is paramagnetic, from the system.

Preparation of $Mn_2P_2O_7$. The $Mn_2P_2O_7$ used in the susceptibility measurements was prepared according to the procedure used in the gravimetric determination of manganese (13). Analytically pure $MnSO_4$ was dissolved in a slightly acidic solution. Diammonium hydrogen phosphate and ammonium chloride were added and the solution was then heated to near its boiling point. Ammonium hydroxide was added to precipitate the manganese as manganese ammonium phosphate. The solution was filtered

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and the precipitate ignited at 1050°C to $Mn_2P_2O_7$. The manganese pyrophosphate obtained was a fine powder light pink in color. The x-ray powder diffraction pattern obtained was in agreement with the one reported in the literature (8).

RESULTS AND DISCUSSION

The susceptibility of a sample of $Mn_2P_2O_7$ was determined from 296°K to 1165°K using fields from 550 to 2850 oersteds. From the data obtained the susceptibility per gram atom of Mn was calculated and a correction applied for the diamagnetism of the constitutent ions (1). The susceptibility was found to be independent of field over the entire temperature range. A graph of the reciprocal gram atomic susceptibility versus temperature is shown in Figure 1. From the graph the Curie constant was calculated to be 4.57, the Weiss constant —14°. The indetermination in C_m is estimated to be less than 1%, while the Weiss constant, which is very sensitive to small variations in C_m, has an indetermination of 10°.

C_m is greater than the value of 4.39, which would be predicted for an ideal system with 5 unpaired electrons per gram atom. Foex and Brunet (9), who made the most extensive measurements previously reported in the literature obtained a value of 4.57 for C_m and —22.5° for Θ.

The value of 4.57 for C_m leads to a magnetic moment of 6.02 Bohr magnetons which in a spin only system would require 5.12 unpaired electrons instead of the hypothetical 5.00. Although the difference is not large, it is felt that it lies well outside of the range of experimental error and that $Mn_2P_2O_7$ must be classified in the group of substances whose magnetic behavior needs further theoretical clarification.

$Mn_2P_2O_7$ is a substance easily prepared in a pure state with a gram susceptibility at room temperature larger than that of most paramagnetic substances. It seems very suitable for use as a susceptibility standard in spite of its abnormal Curie constant. The linear relation between reciprocal susceptibility and temperature is well established so that corrections for small temperature differences can be made. More precise measurements on the susceptibility of $Mn_2P_2O_7$ around room temperature are planned in this laboratory with this view in mind.