

MnWO₄, CALORIMETRIC STUDY OF THE BIFURCATED ANTIFERROMAGNETIC ANOMALY*

Christopher P. Landee[§] and Edgar F. Westrum, Jr., Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104.

ABSTRACT

The heat capacity of a powdered MnWO₄ sample has been measured from 5 - 350 K. The data show three anomalies below 20 K: a small peak at 6.8 ± 0.1 K, then two large sharp peaks at 12.57 ± 0.05 and 13.36 ± 0.05 K. The magnetic entropy was measured as $R \ln 6$. The data between 5 and 11.5 K obeys a power law dependence $C_{mag} = AT^B$ where $B = 1.73$. The sharp double peak is similar to the bifurcated anomaly in MnCl₂ which originates from two distinct antiferromagnetic phases, reported by R. B. Murray *et al.* The double anomaly is discussed in terms of the superexchange properties of MnWO₄.

INTRODUCTION

In the course of determination on the heat capacities of the antiferromagnetic first-row transition metal tungstates,^{1,2} the heat capacity of MnWO₄ has been measured adiabatically from 4 - 350 K.

The structure of manganese tungstate (isostructural with ferrous, cobalt, nickel, and zinc tungstates³) is characterized by zigzag chains of metal filled oxygen octahedra aligned along the c-axis. The crystal structure of the isomorph FeWO₄ is shown in figure 1.

While ferrous, cobalt, and nickel tungstates possess a common magnetic structure with ferromagnetic ordering within the chains and antiferromagnetic alignment of layers,^{4,5} the magnetic structure of manganese tungstate is considerably more complicated with 32 manganese ions in the magnetic unit cell.⁶ Half of the MnWO₄ magnetic unit cell is depicted in figure 2.

EXPERIMENTAL

The sample of MnWO₄ purchased from Rocky Mountain Research was nearly amorphous but after compression into a pellet and firing at 1100 °C for one day X-ray diffraction analysis revealed a sharp, strong pattern with only MnWO₄ lines. Hence, the calorimetric sample was prepared by pressing the pellet, removing the top and bottom surfaces and firing in a platinum crucible for five days at 1100 °C. The surface was again removed after firing and the pellet itself broken into pieces small enough to fit into the calorimeter. No impurity lines were detected in the diffraction analysis and the lattice parameters were in excellent accord with literature values. Chemical analysis for major constituents was in good accord with the theoretical values; less than 40 ppm iron was detected as an impurity. The 85 g sample was prepared in a single batch.

Measurements were made in the Mark II adiabatic cryostat which utilized a gold-plated OFHS copper calorimeter vessel. All calibrations of this instrument are ultimately referred to measurements made at the National Bureau of Standards.

In terms of the Lindemann melting formula, zinc tungstate would be expected to be a good estimate of the lattice contribution for manganese tungstate. A comparison of the respective Debye thetas and their ratios confirm this prediction, for above 120 K the ratio is very constant and near unity out to the highest temperatures measured for the manganese compound. The ratio begins to rise as the temperature drops below 125 K and then drops even more sharply at 65 K as magnetic heat capacity affects the theta for MnWO₄. Since Debye theory predicts a ratio of the thetas equal to the square root of the inverse atomic weights of the cations ($= 1.091$), this value was chosen as the low-temperature limit of the

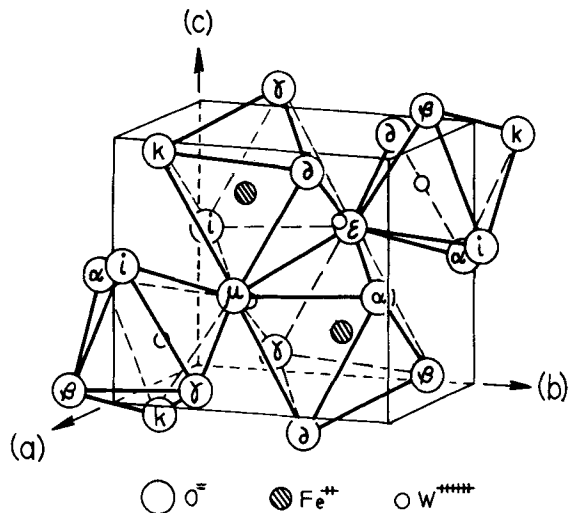


Fig. 1. Crystallographic unit cell of NiWO₄-type tungstates (after Ulku⁵).

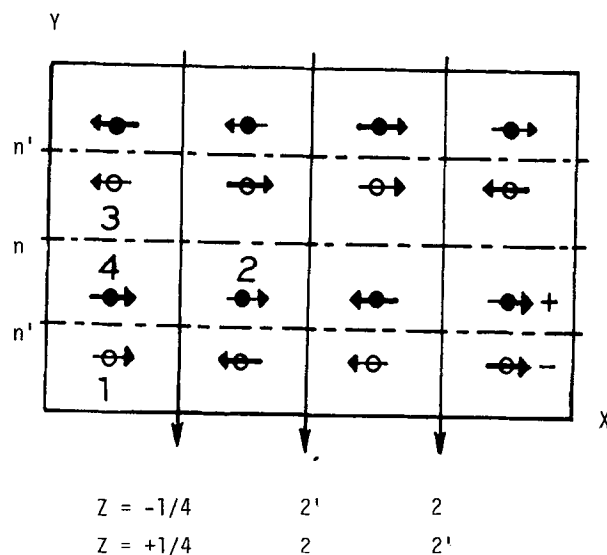


Fig. 2. Magnetic structure of manganese tungstates (cf. Duchs⁷ -- only one-half of the magnetic cell is shown).

ratio curve and a smooth interpolation between this lower value and the experimental ratios above 65 K adopted.

RESULTS AND DISCUSSION

Low-temperature heat capacity data on a granular sample of manganese tungstate is shown in figure 3. There is a small peak at (6.8 ± 0.1) K and a large, bifurcated anomaly with peaks at (12.57 ± 0.05) K and (13.36 ± 0.05) K.

Using the heat capacity data of ZnWO₄ as the basis for a lattice contribution, the magnetic entropy was evaluated for MnWO₄ and found to be $R \ln 6$, characteristic of spin disordering for an $S = 5/2$ system.

A logarithmic plot of the data (figure 4) reveals a power-law dependence of the magnetic heat capacity upon temperature over the range 4 - 11.5 K, excluding the region immediately about the 6.8 K peak. The

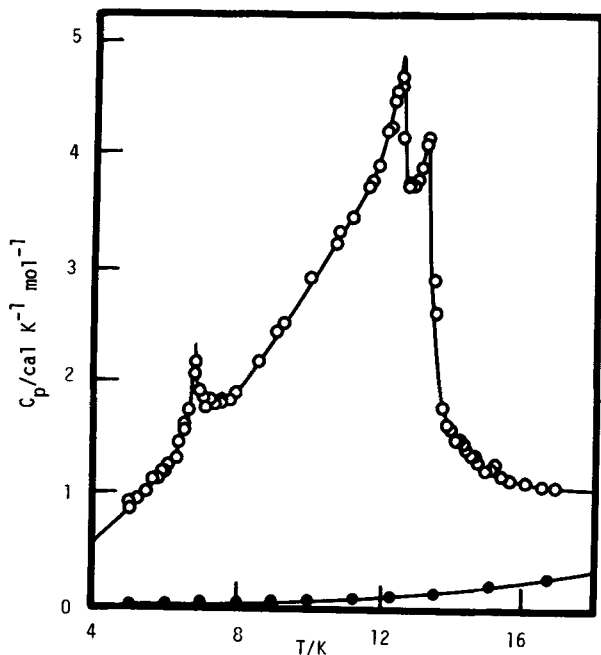


Fig. 3. Low-temperature heat capacity of manganese and zinc tungstates. MnWO_4 —○— and ZnWO_4 —●—

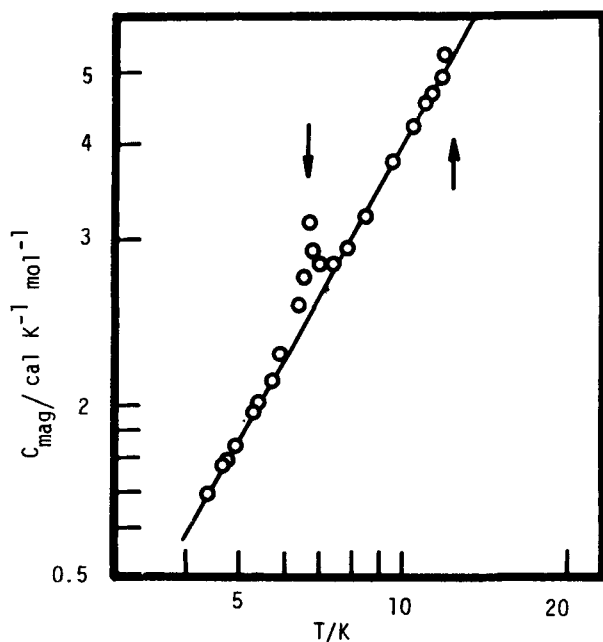


Fig. 4. $\ln C_{\text{mag}}$ vs. $\ln T$ for MnWO_4 .

relationship found was

$$C_{\text{mag}} = 0.052 T^{1.73}$$

The bifurcation of the main peak is considered to be characteristic of manganese tungstate and not particular to the sample measured. General material defects have the property of lowering and broadening the heat capacity of a magnetic transition, but the 12.57 K peak is higher and as sharp as the 13.36 K peak. Weitzel's discoveries of two simultaneous types of magnetic order in mixed crystals of $(\text{Mn}, \text{Fe})\text{WO}_4$ ^{7,9} made it important to check for iron contamination of the sample but a spectroscopic examination revealed

only 40 ppm iron impurity, three orders of magnitude less than would be required to separate the peaks by the amount observed.

The tungstate series, MWO_4 , shares structural and magnetic similarities with the series of transition metal dichlorides, MCl_2 . In both series the metal ions occupy octahedral holes in closest-packed lattices of anions.¹⁰ The nn exchange is over intervening anions with 90° angles. For such arrangements, the Goodenough-Kanamori rules predict ferromagnetic exchange for Fe^{2+} - Fe^{2+} , Co^{2+} - Co^{2+} , and Ni^{2+} - Ni^{2+} but antiferromagnetic exchange for Mn^{2+} - Mn^{2+} .¹¹ The magnetic structures of the dichlorides are similar to those of the tungstates mentioned above; the iron, cobalt, and nickel compounds have ferromagnetic layers coupled antiferromagnetically to adjacent layers. In MnCl_2 , the spins are ordered in a more complicated manner within each layer.¹²

In MnCl_2 , the low-temperature maxima in the heat capacity is also bifurcated with the twin peaks occurring at 1.81 and 1.96 K.¹³ Neutron diffraction experiments revealed the presence of two distinct AFM-phases at low temperatures;¹² the peaks in the heat capacity correspond to the phase transitions $\text{AFMII} \rightarrow \text{AFMI} \rightarrow \text{PM}$.

The similarity of the 90° superexchange and the bifurcation of the heat capacity anomalies in MnCl_2 and MnWO_4 suggest several low-temperature magnetic phases in manganese tungstate.

A more complete account of this work will appear in the Journal of Chemical Thermodynamics.

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 § Present address: Department of Chemistry, Washington State University, Pullman, Washington 99163.
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