JOURNAL OF SOLID STATE CHEMISTRY 17, 323–325 (1976)

The Magnetic Structure of Ba_2MnWO_6*

C. P. KHATTAK AND D. E. COX

Brookhaven National Laboratory†, *Upton, New York 11973*

AND

F. F. Y. WANG

Department of Materials Science, SUNY at Stony Brook, New York 11794

Received November 12, 1975

Powder neutron diffraction and magnetic measurements have shown that the ordered perovskite Ba_2MnWO_6 is antiferromagnetic with a Néel temperature of 7.5 ± 1°K. Below this temperature, ordering of the second kind occurs, with the Mn moments directed perpendicular to the [111] axis.

Introduction

Recent magnetic and neutron diffraction measurements on ordered barium perovskites have revealed a variety of magnetic structures, ranging from antiferromagnetic in Ba_2CoWO_6 and Ba_2NiWO_6 (*1*, *2*), ferrimagnetic in Ba_2MnReO_6 (*3*, *4*), and a spiral arrangement in Ba_2CoReO_6 (*5*). The ordered perovskites are derived from the normal ABO_3 perovskites when two types of B cations are present with suitably different size and charge. In this case, the B and B' cations order on alternate (111) layers, the basic cubic perovskite cell is doubled along all three axes and the lattice becomes face-centered cubic. A slight distortion of the oxygen lattice also occurs, but the octahedral symmetry of the B sites is retained.

The antiferromagnetic structure of Ba_2CoWO_6 and Ba_2NiWO_6 consists of ordering of the second kind, in which next-nearest-neighbor Co or Ni moments are coupled antiparallel. In Ba_2MnReO_6, the Mn and Re moments are believed to be coupled antiparallel (*3*), leading to a ferrimagnetic structure, although neutron diffraction experiments were unable to detect a localized moment on the Re ions (*4*). The present work describes a neutron diffraction study on polycrystalline Ba_2MnWO_6. The results show that there is also ordering of the second kind in this compound, consistent with Blasse's predictions (*1*) concerning superexchange in these materials.

Sample Preparation and Magnetic Measurements

A polycrystalline sample of Ba_2MnWO_6 was prepared by heating appropriate "Baker-analyzed" grade carbonates and WO_3 in a nitrogen atmosphere at 1250°C. The material thus obtained was reground and annealed in a sealed, evacuated, silica capsule at 800°C for 3 days. An X-ray pattern of this material in an IRD-Guinier camera obtained with copper $K\alpha_1$ radiation showed a face-centered cubic structure with a lattice parameter of 8.19_3 Å.

---

* By acceptance of this article the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper.

† Work at Brookhaven performed under the auspices of the U.S. Energy Research and Development Administration.

11**

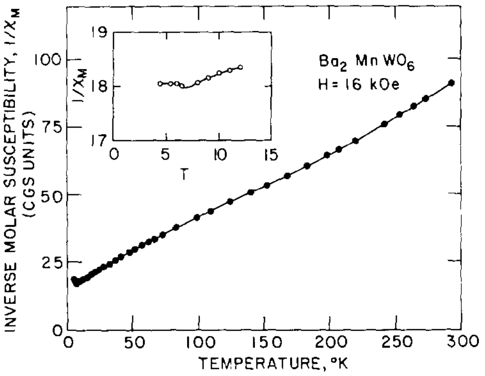

FIG. 1. Inverse molar susceptibility, $1/\chi_M$, plotted against temperature for polycrystalline Ba_2MnWO_6. The inset shows the low temperature region in greater detail.

One weak impurity line corresponding to the most intense peak of $BaWO_4$ was also observed.

Magnetic susceptibility measurements on polycrystalline Ba_2MnWO_6 were made in the temperature range 4.2°K to 300°K. The inverse molar susceptibility, $1/\chi_M$, vs temperature plot is shown in Fig. 1. The material exhibited antiferromagnetic behavior with a Néel temperature of 7.5 ± 1°K. From the roughly linear portion in the high temperature region the Curie–Weiss constant, θ_0, was calculated to be −36°K, and the effective moment, μ_{eff}, 5.4 ± 0.2 μ_B per formula unit.

Magnetic Structure Determination

Neutron diffraction data were taken at 20°K and 4.5°K with 2.366 Å wavelength neutrons. The former were used for analysis of the crystal structure, described by the space group *Fm*3*m* (O_h^5), with Ba in 8(*c*) positions at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$); Mn in 4(*a*) at (0, 0, 0); W in 4(*b*) at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$); and O in 24(*e*) at (*x*, 0, 0). The ideal value of the oxygen parameter, *x*, is 0.25 as realized in the simple perovskite structure. The neutron pattern revealed that in addition to some small $BaWO_4$ peaks, there were some other small peaks which could be attributed to the 15-layered structure of a slightly oxygen deficient phase of $BaMnO_3$ (*6*). An estimate of the impurity content from the scattering data gave a value of about 5 mole% each for $BaWO_4$ and $BaMnO_3$.

The results of a least-squares refinement of the data after making the necessary correction for scattering due to the impurities is shown in Table I. The weighted *R* factor is defined as

$$[\sum w(I_{obsd} - I_{calcd})^2 / \sum w(I_{obsd})^2]^{1/2}$$

where $w = 1/\sigma^2$, σ being the error assigned to each observation. An order parameter, *S*, defined as the fraction of Mn ions on B, i.e.,

TABLE I

OBSERVED AND CALCULATED NUCLEAR INTENSITIES FOR Ba_2MnWO_6 AT 20° K[a]

h k l	I_{obsd}	I_{calcd}
(1 1 1)	73	74
(2 0 0)	2	2
(2 2 0)	0	0
(3 1 1)	46	26
(2 2 2)	295	284
(4 0 0)	173	179
(3 3 1)	3	3
(4 2 0)	1	1
Weighted *R* factor		0.069

[a] Data have been corrected for small impurity contents of $BaWO_4$ and $BaMnO_3$ as mentioned in text. Scattering amplitudes 0.512, −0.387, 0.48, 0.5803 × 10^{-12} cm for Ba, Mn, W, and O, respectively (*7*).

TABLE II

OBSERVED AND CALCULATED MAGNETIC INTENSITIES FOR Ba_2MnWO_6[a]

h k l	I_{obsd}	I_{calcd}	
		ϕ=90°	ϕ=75°
($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)	73	74	72
($\frac{3}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)	29	26	28
($\frac{3}{2}$ $\frac{3}{2}$ $\frac{1}{2}$)	17	18	18
($\frac{3}{2}$ $\frac{3}{2}$ $\frac{3}{2}$), ($\frac{5}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)	16	18	17
($\frac{5}{2}$ $\frac{3}{2}$ $\frac{1}{2}$)	11	12	12
Weighted *R* factor		0.069	0.052

[a] The experimentally determined form factor for Mn^{2+} has been used (*8*). $\mu_{Mn} = 4.2 \pm 0.1\ \mu_B$. ϕ is the angle between moment direction and (111) axis.

4(*a*) sites, the oxygen parameter, x, and a scale factor were used as the variables in the refinement. The final values obtained were $S = 0.98 \pm 0.02$ and $x = 0.265 \pm 0.001$, similar to values reported for the related compounds previously studied.

The neutron data at 4.5°K revealed additional scattering compared to the 20°K data. The intensity of the strongest of these additional peaks was found to fall to zero around 8.3°K, confirming it to be magnetic in origin. The contribution due to magnetic scattering could be indexed on the basis of a cell double that of the chemical cell along all three edges, with *hkl* indices all odd, characteristic of ordering of the second kind. A least-squares refinement of the magnetic peaks shown in Table II, with the moment of the Mn ion as variable and the spin direction perpendicular to the [111] axis yielded a moment of 4.2 ± 0.1 μ_B per Mn ion at 4.5°K. A slightly better fit was obtained with the spin directed about 75° from the [111] axis, but the data are not accurate enough for this to be regarded as significant. The low value of the Mn moment most likely reflects the proximity of the Néel temperature.

The above results are consistent with Blasse's predictions concerning superexchange through two oxygen anions in these materials (*9*) and also with his argument that the valency states in ordered Mn–W perovskites are Mn^{2+}–W^{6+} rather than Mn^{3+}–W^{5+}.

References

1. G. Blasse, Proceedings of the International Conference on Magnetism, Nottingham, England (1964).

2. D. E. Cox, G. Shirane, and B. C. Frazer, *J. Appl. Phys.* **38**, 1459 (1967).

3. A. W. Sleight and J. F. Weiher, *J. Phys. Chem. Solids* **33**, 679 (1972).

4. C. P. Khattak, D. E. Cox, and F. F. Y. Wang, *J. Solid State Chem.* **13**, 77 (1975).

5. C. P. Khattak, D. E. Cox, and F. F. Y. Wang, A.I.P. Conference Proceedings, No. 10, 674 (1972).

6. T. Negas and R. S. Roth, *J. Solid State Chem.* **3**, 323 (1971).

7. C. G. Shull, "Coherent Neutron Scattering Amplitudes," Massachusetts Institute of Technology, Cambridge, Massachusetts (1972).

8. L. M. Corliss, N. Elliott, and J. M. Hastings, *Phys. Rev.* **104**, 924 (1956).

9. G. Blasse, *J. Inorg. Nucl. Chem.* **27**, 993 (1965).