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Hydrothermal and High-Pressure Preparation of Some $BaMnO_3$ Modifications and Low-Temperature Magnetic Properties of $BaMnO_3(2H)$

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Three modifications of barium manganese oxide, $BaMnO_3(2H)$, $BaMnO_3(9R)$, and $BaMnO_3(4H)$, were prepared using hydrothermal and high-pressure techniques. The crystal structure of $BaMnO_3(2H)$ was refined using X-ray and neutron-diffraction powder patterns. The structure is hexagonal with space group $P6_3mmc$, and $a = 5.694$ Å, $c = 4.806$ Å.

The magnetic properties of $BaMnO_3(2H)$ were investigated between 2.4° and 273°K in a magnetic field of 9750 Oe. The compound is antiferromagnetic with a Néel temperature of less than 2.4°K. Neutron-diffraction powder patterns were obtained at 1.8°K and 300°K. Three weak magnetic superlattice reflections were indexed on the basis of a hexagonal unit cell with the dimensions $a_H = a\sqrt{3}$, and $c_H = c$, where a and c are the dimensions of the chemical unit cell. A collinear antiferromagnetic arrangement of the spins parallel to the [001] direction describes the magnetic structure.

Barium manganese oxide is polymorphic. The compound has at room temperature a two-layer hexagonal $BaNiO_3$ structure (*1*), $BaMnO_3(2H)$, (*2*). This modification is formed, when the compound is prepared by hydrothermal synthesis at temperatures below 330°C and at pressures up to 600 atm (*3*). A four-layer hexagonal structure (*2*), $BaMnO_3(4H)$, also found in $BaCrO_3$ (*4*), is obtained when the compound is prepared by ignition of $BaMnO_4$ at 1150°C (*2*), or prepared from $BaMnO_3(2H)$ at 1200°C at a pressure of 90 kbar (*5, 6*). A nine-layer rhombohedral structure, $BaMnO_3(9R)$, with a crystal structure similar to that of $BaRuO_3$ (*7*) is obtained, when the compound is prepared by high-pressure synthesis from $BaMnO_3(2H)$ at pressures up to 75 kbar and temperatures up to 1300°C (*5, 6*). This modification is also obtained when the compound is prepared hydrothermally at temperatures from 325° to 440°C and pressures from 100 to 600 atm (*3*), or at 700°C and 3000 atm (*6*).

$BaMnO_3(2H)$ is obtained in the temperature range from 500° to 1000°C by ignition of barium manganate, $BaMnO_4$, using dry, oxygen-free nitrogen as a protective atmosphere (*8*). Solid state reactions of BaO–MnO_2 mixtures or ignition of $BaMnO_4$ in air yield black products of $BaMnO_3(2H)$, which are nonstoichiometric according to chemical analysis (*5, 6*). Stoichiometric $BaMnO_3(2H)$ is obtained by hydrothermal synthesis from freshly precipitated manganese IV oxide in a barium hydroxide solution (*3*). The product so prepared is green.

A structure similar to that of $BaNiO_3$ (*1*) has been suggested for $BaMnO_3(2H)$ (*2*). However, the structure has not been refined. The crystal structure, the low-temperature magnetic properties, and the magnetic structure of hydrothermally prepared stoichiometric $BaMnO_3(2H)$ are reported below.

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TABLE I

EXPERIMENTAL CONDITIONS FOR HYDROTHERMAL PREPARATION OF BARIUM MANGANESE OXIDE

Exp. No.	Temp., °C	Pressure, atm	Time, hr	Product
1	275	50	24	$BaMnO_3$(2H)
2	420	600	34	$BaMnO_3$(9R)

Experimental

Chemistry

Barium manganese oxide was prepared hydrothermally in a 100-ml pressure bomb lined with pure silver. Manganese IV oxide was prepared from a boiling solution of 2 g $KMnO_4$ in 400 ml of carbon-dioxide-free water by reduction with 10 ml of ethyl alcohol. The precipitate was washed by decantation with 400 ml of hot carbon-dioxide-free water, was isolated by filtration, and was used immediately. In a typical hydrothermal experiment the freshly prepared precipitate of manganese IV oxide was treated with a mixture of 10 g freshly recrystallized barium hydroxide, $Ba(OH)_2.8H_2O$, 2 g barium peroxide, BaO_2, and 40 ml of carbon-dioxide-free water at the experimental conditions given in Table I. The product was washed with 400 ml of carbon-dioxide-free water and was dried in air at 25°C. The product from experiment no. 1 is green, stoichiometric $BaMnO_3$(2H), but contains small amounts of barium carbonate. The product from experiment no. 2 is black, and is $BaMnO_3$(9R). Manganese was determined by EDTA titration and active oxygen was determined by iodine thiosulphate titration. (Found for $BaMnO_3$(2H): active O/Mn 0.998. Calc. for $BaMnO_3$: active O/Mn 1.000.) A high-pressure belt apparatus (*9*) was used in high-pressure preparations of $BaMnO_3$(9R) and of $BaMnO_3$(4H) at the experimental conditions shown in Table II. The starting material, $BaMnO_3$(2H), was placed in platinum ampoules with a volume of 26 mm^3.

TABLE II

EXPERIMENTAL CONDITIONS FOR HIGH-PRESSURE PREPARATION OF $BaMnO_3$(9R) AND $BaMnO_3$(4H)

Exp. No.	Temp., °C	Pressure, kbar	Time, hr	Initial condition	Product
1	500	20	1	$BaMnO_3$(2H)	$BaMnO_3$(9R)
2	500	55	1	$BaMnO_3$(2H)	$BaMnO_3$(9R)
3	500	100	1	$BaMnO_3$(2H)	$BaMnO_3$(4H)

X-Ray Technique

The powder pattern of hydrothermally prepared $BaMnO_3$(2H) and of $BaMnO_3$(9R) were obtained with a Guinier–de Wolff camera using Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å, and sodium chloride as an internal standard, $a_{NaCl} = 5.6389$ Å. The powder patterns of $BaMnO_3$(9R) and of $BaMnO_3$(4H) obtained by high-pressure synthesis were taken with a Guinier camera using Fe$K\alpha_1$ radiation, $\lambda = 1.9359$ Å. No internal standard was used. The powder patterns of the three polymorphs have been reported previously (*5*). The powder pattern of $BaMnO_3$(2H) was indexed with a hexagonal cell (see Table III). From the powder pattern the unit cell parameters were calculated using a least-squares program (*10*) (see Table IV). For comparison some previously reported values are listed as well. The preparation of $BaMnO_3$(2H), Table I no. 1, was repeated ten times in order to prepare a sample for a neutron-diffraction investigation, and Guinier

TABLE III

OBSERVED AND CALCULATED INTERPLANAR SPACINGS IN Å AND INTENSITIES OF $BaMnO_3$(2H)[a]

$h\,k\,l$	d_{obs}	d_{calc}	jF_o^2	jF_c^2
1 0 1	3.447	3.442	80	68
1 1 0	2.847	2.847	93	89
2 0 0	2.466	2.466	8	4
0 0 2	2.402	2.403	17	15
2 0 1	2.194	2.194	152	126
1 0 2	2.161	2.160	48	63
1 1 2	1.837	1.836	26	19
2 1 1	1.737	1.738	82	88
2 0 2	1.722	1.721	68	86
3 0 0	1.645	1.644	57	62
1 0 3	1.525	1.524	38	43
2 1 2	1.473	1.473	86	105
2 2 0	1.424	1.424	81	91
3 0 2	1.357	1.357	18	16
2 0 3	1.344	1.343	44	75
3 1 1	1.316	1.315	79	79
2 2 2	1.225	1.225	27	41
2 1 3	1.216	1.215	24	67
0 0 4	1.203	1.201	7	24
4 0 1	1.193	1.194	53	64
3 1 2	1.188	1.189	43	75

[a] $R = \sum |jF_o^2 - kjF_c^2| / \sum jF_o^2 = 17\%$. j is the multiplicity, F is the structure factor, and k is a scaling factor. $a = 5.694$ Å, $c = 4.806$ Å.

TABLE IV

UNIT CELL PARAMETERS OF $BaMnO_3$(2H) IN Å; STANDARD DEVIATIONS IN PARENTHESES

Ref.	2	5	6	This work
a	5.672(4)	5.675(1)	5.695	5.694(2)
c	4.71(1)	4.708(3)	4.812	4.806(1)

powder patterns were taken of the products from each preparation. The pattern indicated in some cases weak lines of barium carbonate. Intensities of 21 lines in the powder pattern were measured with an automatic powder diffractometer, using Fe$K\alpha_1$-radiation, $\lambda = 1.9359$ Å, monochromated by reflection from the $(10\bar{1}0)$ plane of a quartz crystal. Lorentz polarization correction was applied using the function

$$LP(\theta) = (1 + \cos^2 2\alpha \cdot \cos^2 2\theta)/2 \sin^2 \theta \cdot \cos \theta,$$

where α is the Bragg angle of the monochromator (16.85°). No absorption correction was made. The observed intensities $j \cdot F_o^2$, where j is the multiplicity of the reflection and F_o is the structure factor, are shown in Table III.

Magnetic Measurements

The magnetization of $BaMnO_3$(2H) was measured at temperatures from 2.3°K to 273°K in a magnetic field of 9750 Oe using a translation balance. Figure 1 shows the magnetization per gram *vs* temperature, and Fig. 2 shows the inverse molar susceptibility *vs* temperature. The compound probably has a magnetically ordered state close to 2.3°K. The magnetization was measured at 1.6°K and 4.2°K in magnetic fields up to 80 KOe using the axial extraction method. Figure 3 is a plot of magnetization *vs* field. The susceptibility is field dependent.

Neutron Technique

The neutron diffraction powder pattern of $BaMnO_3$(2H) was measured at room temperature and at 1.8°K by a neutron diffractometer at Centre d'Etudes Nucleaires Grenoble, using 1.154-Å neutrons. The sample was placed in a cylindrical vanadium container of 15 mm diameter. The powder pattern showed some weak reflections from barium carbonate. From the intensities of these reflections and those of $BaMnO_3$(2H) a barium carbonate content of approximately 5% has been estimated. The room temperature pattern was indexed on the basis of the chemical unit cell, and Lorentz correction was applied,

$$LP(\theta) = 1/\sin \theta \cdot \sin 2\theta$$

(Table V). The powder pattern taken at 1.8°K showed three rather weak superstructure lines. All the magnetic reflections were indexed using a hexagonal cell with $a_H = a\sqrt{3}$ and $c_H = c$, where a and c are the unit cell parameters of the chemical cell, and Lorentz correction was applied (Table VI).

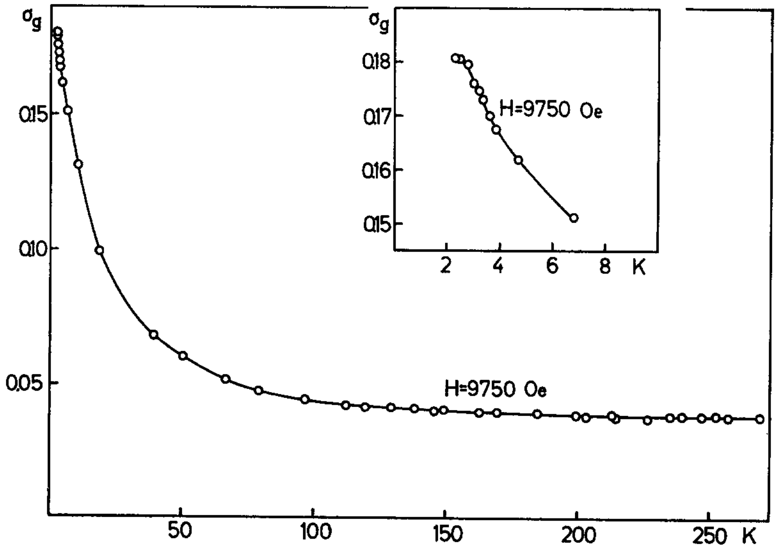

FIG. 1. The magnetization per gram in emu versus the temperature for $BaMnO_3$(2H) at 9750 Oe.

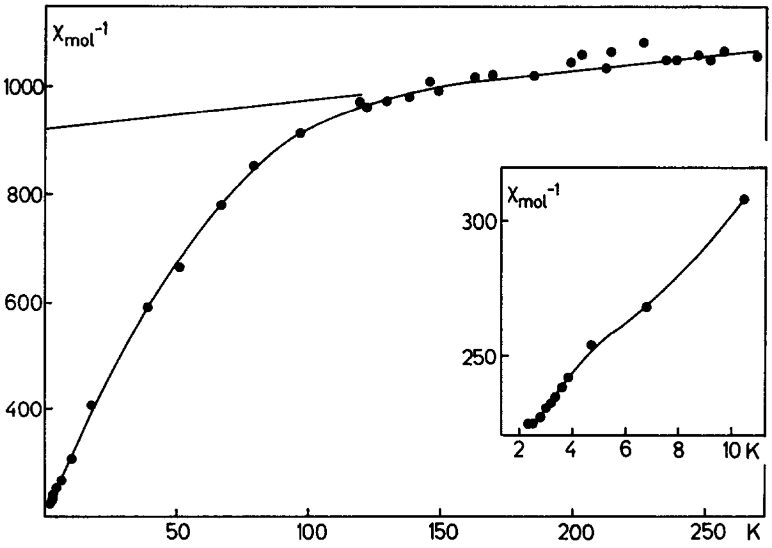

FIG. 2. The inverse molar susceptibility versus the temperature.

Crystal Data and Structure Refinement

$BaMnO_3$(2H) is hexagonal with space group $P6_3mmc$, No. 194. Six oxygen atoms occupy site *h*, two barium atoms occupy site *d*, and two manganese atoms occupy site *a*. The unit cell contains two formula units. The cell parameters are in Table IV.

Intensities of sixteen lines from the X-ray powder pattern were used in the refinement of the coordinates of the oxygen atom, using the least squares program AFI (*11*). Temperature factors were not included in the refinement. Table VII shows the coordinates obtained at the end of the refinement at an R-value of 17 %, and Table III gives the calculated intensities. The structure was also refined using the noncentrosymmetrical space group $P6_3mc$, No. 186, suggested previously (*2*). However, this gave *z* coordinates for the oxygen and the barium atoms which did not correspond to a meaningful structure.

Intensities of thirteen lines from the neutron powder pattern taken at room temperature were used in the refinement of the coordinates of the oxygen atom, using the least-squares program AFM (*11*). The thermal parameters were not included in the

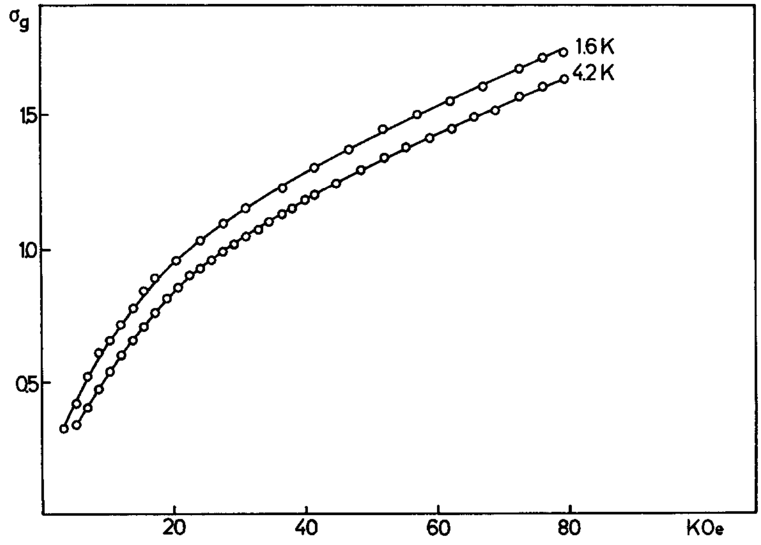

FIG. 3. The magnetization per gram in emu versus field at 1.6°K and 4.2°K.

TABLE V

Observed and Calculated Intensities of the Room Temperature Diagram of $BaMnO_3(2H)$[a]

h k l	jF_o^2	jF_c^2	$\sum jF_c^2$
1 0 0	0.74	0.08	
1 0 1	0.22	0.45	
1 1 0	3.47	2.49	
2 0 0	108.43	47.90	102.44
0 0 2		54.54	
2 0 1	195.66	163.61	184.74
1 0 2		21.13	
2 1 0	38.64	35.65	43.24
1 1 2		7.59	
2 1 1	28.00	8.49	31.53
2 0 2		23.04	
3 0 0	3.71	6.10	
3 0 1	39.52	37.02	37.47
1 0 3		0.45	
2 1 2	0.89	1.93	
2 2 0	53.80	56.01	
1 3 0	174.60	3.74	183.78
3 0 2		2.24	
2 0 3		163.61	
3 1 1		14.19	
4 0 0	446.25	41.96	447.53
2 2 2		242.48	
2 1 3		8.49	
0 0 4		28.61	
4 0 1		107.18	
3 1 2		18.66	
1 0 4		0.15	

[a] $R = \sum |jF_o^2 - kjF_c^2| / \sum jF_o^2 = 4.1\%$. *j* is the multiplicity, *F* is the structure factor, and *k* is a scaling factor.

refinement. Table VII shows the coordinates obtained at the end of the refinement at an R-value of 4.1%. The calculated intensities are listed in Table V. The atomic scattering amplitudes of oxygen, manganese, and barium are 0.577, –0.36, and 0.52 ($\times 10^{-12}$ cm) respectively (*12*). The space group *P*6_3*mmc* was applied. Refinement of the structure using the noncentrosymmetrical space group *P*6_3*mc* gave coordinates of the oxygen atom that were within one standard deviation of the coordinates listed in Table VII, and gave coordinates of the barium atom deviating a little more than two standard deviations from the coordinates of Table VII. Thus it is concluded that the structure of $BaMnO_3(2H)$ is best described by using the space group *P*6_3*mmc*.

TABLE VI

Observed and Calculated Magnetic Reflections for $BaMnO_3(2H)$. $a_H = 9.864$ Å, $c_H = 4.806$ Å

h k l	I_{obs}	σI_{obs}	I_{calc}
1 0 1	2.44	0.2	2.31
2 0 1	3.90	0.5	4.16
2 1 1	4.80	1.6	8.00

TABLE VII

Atomic Coordinates

X-Ray Data, $R = 17\%$

Atom	*x*	*y*	*z*
O	0.158(11)	0.316(22)	1/4
Mn	0	0	0
Ba	1/3	2/3	3/4

Neutron Data, $R = 4.1\%$

Atom	*x*	*y*	*z*
O	0.1450(6)	0.2900(12)	1/4
Mn	0	0	0
Ba	1/3	2/3	3/4

Magnetic Structure

$BaMnO_3(2H)$ is antiferromagnetic. The volume of the magnetic cell is three times that of the chemical cell, and the cell contains six manganese atoms. Each manganese atom has two nearest manganese atoms perpendicular to the basal plane at a distance of 2.403 Å. In the basal plane, each manganese atom has six nearest manganese atoms at a distance of 5.694 Å. The structure consists of MnO_6 octahedra stacked in the *c* direction by sharing triangular surfaces; see Figs. 4 and 5. The following model is proposed for an antiferromagnetic arrangement of the magnetic spins: A linear model with the spin axis parallel to the *c* axis. The spin of the manganese atom at the position (0,0,0) is opposite to the spin of the manganese atoms at the positions (1/3,2/3,0) and (2/3,1/3,0) (see Fig. 6 and Table VIII). This model gave a good agreement between observed and calculated magnetic intensities. The observed magnetic intensities are small and their standard deviations are listed in Table VI. The magnetic structure factor for a reflection *hkl* is proportional to

$$\mathbf{F}_{hkl} = \Sigma_i S_i \mathbf{q}_i \exp 2\pi i (hx_i + ky_i + lz_i).$$

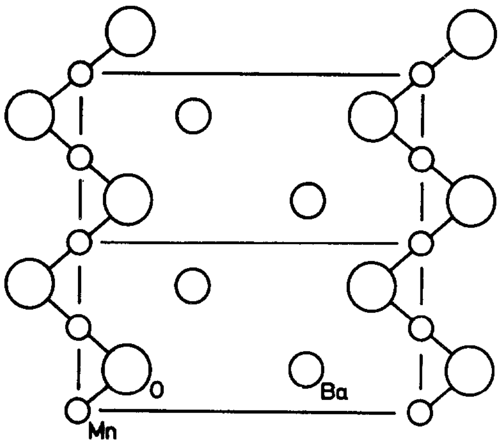

FIG. 4. Atoms in the (110) plane of the chemical unit cell.

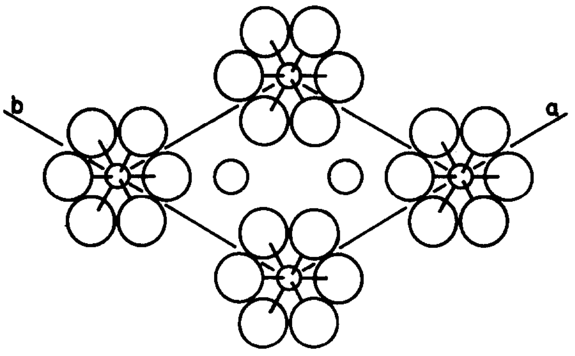

FIG. 5. Projection of atoms with $z = 1/4$, $1/2$, and $3/4$ on the basal plane.

TABLE VIII

ATOMIC COORDINATES AND SPINS OF THE SIX MANGANESE ATOMS IN THE MAGNETIC CELL

Atom no.	x	y	z	Spin
1	0	0	0	S
2	1/3	2/3	0	$-S$
3	2/3	1/3	0	$-S$
4	0	0	1/2	$-S$
5	1/3	2/3	1/2	S
6	2/3	1/3	1/2	S

Using the coordinates and spins of Table VIII and taking into account that $l = 2n + 1$ for all the observed magnetic reflections, the magnetic structure factor is:

$$\begin{aligned} \mathbf{F}_{hkl} &= 2q\mathbf{S}(1 - \exp 2\pi i(h + 2k)/3 \\ &\quad - \exp 2\pi i(2h + k)/3) \\ &= 4q\mathbf{S}. \end{aligned}$$

The intensities of the magnetic reflections are:

$$I_M = pf^2 q^2 (4S)^2 \, 0.27^2 \, A,$$

p	the multiplicity of the reflection,
f	the magnetic form factor of Mn^{4+} (*13*),
q^2	is calculated from a formula in (*14*),
S	the magnetic moment,
A	a scaling factor.

The intensities are shown in Table VI. The magnetic moment of the Mn^{4+} ion determined from the (101)

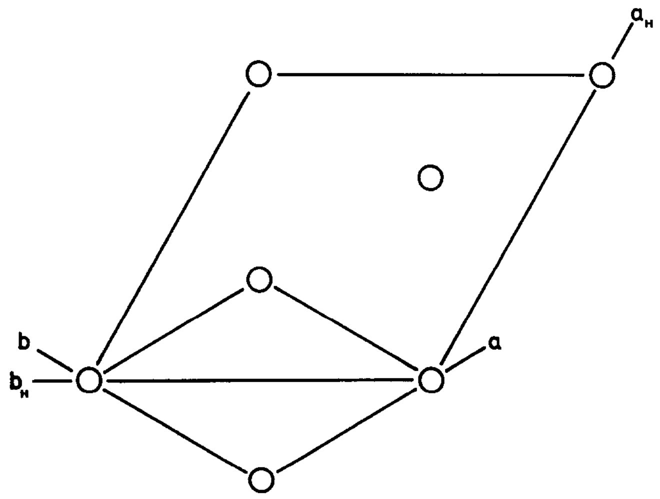

FIG. 6. Relation between the chemical and the magnetic unit cell and positions of the manganese atoms in the magnetic cell. For simplicity all other atoms have been omitted.

reflection is $3 \pm 0.3\mu_B$, in good agreement with the theoretical value.

Discussion

The present investigation shows that stoichiometric $BaMnO_3$(2H) can be prepared by hydrothermal synthesis, and that $BaMnO_3$(9R) also can be obtained by using the hydrothermal technique. The high-pressure transformation of $BaMnO_3$(2H) to $BaMnO_3$(9R) and to $BaMnO_3$(4H) previously reported (*5*, *6*) was confirmed. However, it was possible to prepare $BaMnO_3$(4H) at a much lower temperature (500°C and 100 kbar) than previously reported (*5*, *6*) (1300°C and 75 kbar).

Refinement of the crystal structure of $BaMnO_3$(2H) using X-ray and neutron-diffraction powder patterns showed that the structure suggested by Hardy (*2*) was correct, but the structure is, however, best described with the space group $P6_3mmc$. The structure has a surprisingly short manganese distance of 2.403 Å.

The investigation of the magnetic properties of $BaMnO_3$(2H) showed that the compound most probably has an antiferromagnetically ordered state at temperatures under 2.3°K. From the curve showing the inverse molar susceptibility *vs* temperature, an effective moment of 3.82 was found for the Mn^{4+} ion in good agreement with the theoretical value of 3.89.

The observed molar Curie constant C_M is 1.83. The curve follows the Curie–Weiss equation from 150°K with a paramagnetic temperature $\theta_p = -1700°K$. Investigations of the magnetization of $BaMnO_3$(2H) at 1.6°K and 4.2°K has shown the susceptibility to be field dependent (see Fig. 3).

Triangular models in the basal plane are simply eliminated by a calculated ratio $I(201)/I(101) < 1$ contrary to observation.

The collinear model gives a different nature to the spin in (000) and those in $(\frac{1}{3}\frac{2}{3}0)$ and $(\frac{2}{3}\frac{1}{3}0)$. The cell with the unit cell parameters: $[a\sqrt{3}, a\sqrt{3}, c]$ belongs to space group $P6_3mmc$ and the six manganese atoms split into two different kinds of sites: two manganese spins occupy site *a* surrounded by six neighbours *f* with opposite sign; four manganese spins occupy site *f* surrounded by three neighbours *a* with opposite sign and three neighbours *f* with same sign.

The spin direction is probably determined by uniaxial anisotropy. The dominant exchange coupling of Mn^{4+} spins occurs along the *c* chains. The intrachain separation of neighbouring Mn^{4+} ions is 2.403 Å while the interchain distance is 5.694 Å.

Neutron-diffraction powder patterns taken at 77°K and at 4.2°K show magnetic reflections with increasing intensities. For the magnetic reflection (101) the intensities are 1.02 and 2.40, respectively. The compound could possibly have a partial magnetically ordered state at temperatures below 150°K. Magnetic order in one dimension is a possibility, and further investigations of this are planned.

Acknowledgments

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