

## Magnetic and Optical Investigation of $\text{Mg}_6\text{MnO}_8$

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Magnetic susceptibility measurements and optical reflectance spectra of the pure compound  $\text{Mg}_6\text{MnO}_8$  are reported and discussed. The magnetic moment of  $3.94 \pm 0.08 \mu_B$  and the Weiss temperature of  $-20 \pm 5 \text{ K}$  are consistent with the structure of the compound which has paramagnetic  $\text{Mn}^{4+}$  ions ( $d^3$  configuration) in an octahedral environment with only weak antiferromagnetic interaction. The first spin-allowed  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition has been assigned to the band observed at 20.4 kK; the remaining bands in the reflectance spectrum also have been assigned.

The compound  $\text{Mg}_6\text{MnO}_8$  belongs to a class of substances of general formula  $\text{A}_6\text{BO}_8$  where A and B are 2+ and 4+ cations, respectively. The other members of this class to date known are  $\text{Ni}_6\text{MnO}_8$  (1) and  $\text{Cu}_6\text{PbO}_8$  (2).

The crystal structure of  $\text{Mg}_6\text{MnO}_8$  (2), Fig. 1, is cubic and may be considered as derived from the rock-salt structure of  $\text{MgO}$  by replacing 1/8 of the  $\text{Mg}^{2+}$  cations with  $\text{Mn}^{4+}$  ions and 1/8

with vacancies. The  $\text{Mn}^{4+}$  ions and vacancies occupy (111) alternate lattice layers and are further ordered within the layers such that each  $\text{Mn}^{4+}$  ion has six vacancies in place of the next-nearest cation neighbors. Both the 2+ and 4+ cations are octahedrally coordinated by six oxygen ions. The octahedron around the 4+ ions is regular whereas that around the 2+ ions is distorted.

Several studies of the optical properties of  $\text{Mn}^{4+}$  ions dispersed in host lattices have been reported (3-6), whereas very little is known about the spectroscopic behavior of pure  $\text{Mn}^{4+}$  compounds mainly because of their instability (7, 8). However,  $\text{Mg}_6\text{MnO}_8$  is a convenient compound to deal with since it is very stable, can easily be prepared pure and contains  $\text{Mn}^{4+}$  as a major component instead of being present as impurity ion. These considerations, as well as the characteristic crystal structure described above, have prompted us to investigate the magnetic and optical properties of this compound.

### Experimental Procedure

#### Specimen Preparation.

The sample was prepared according to Wickham (1). A solution of magnesium and manganese acetate (Erba R.P.) in molar ratio 20:1 was prepared. The precipitate obtained by addition of oxalic acid to the boiling solution was filtered, washed, and dried at 105°C. Small

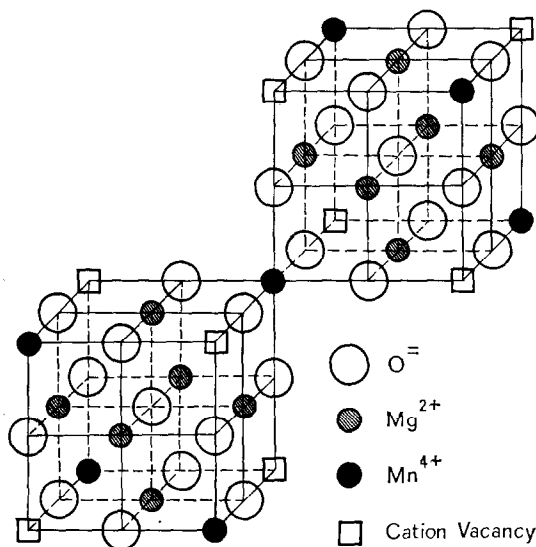


FIG. 1. Crystal structure of  $\text{Mg}_6\text{MnO}_8$  (2). Two octants of the cubic unit cell are shown. For the sake of clarity the dimensions of the unit cell and of the ionic radii are not in the same scale.

portions of this product were calcined from 500 to 1200°C in 100°C steps for a few hours in air. From the X-ray spectra the presence of MgO, Mg<sub>2</sub>MnO<sub>4</sub>, and Mg<sub>6</sub>MnO<sub>8</sub> phases was observed for samples heated at temperatures starting from 900°C, whereas only Mg<sub>6</sub>MnO<sub>8</sub> and MgO were observed to be present for samples calcined at 700 and 800°C. The product dried at 105°C therefore was calcined at 800°C for 3 hr in air. After grinding in a mortar, the powder was washed with a hot 10% solution of NH<sub>4</sub>Cl to remove the excess MgO, filtered, washed with water, and finally dried. To test the purity of the final washed product an X-ray spectrum was run on a powder diffractometer at a very low scanning rate. In this spectrum the 220 reflection of MgO, usually strong in intensity (9) and well resolved from the 440 line of Mg<sub>6</sub>MnO<sub>8</sub> was not visible (with CuK<sub>α</sub> radiation the 220 reflection of MgO has  $2\theta = 62.3^\circ$  and the 440 reflection of Mg<sub>6</sub>MnO<sub>8</sub> has  $2\theta = 62.7^\circ$ ). It may be mentioned that attempts to prepare the pure compound by other methods, described in the literature (2, 10), were unsuccessful.

#### Chemical Analysis.

The total manganese content in the sample was determined spectrophotometrically as permanganate (at  $\lambda = 526$  nm), oxidation to MnO<sub>4</sub><sup>-</sup> being carried out using the periodate method (11). In addition the manganese was also determined oxidimetrically in order to check its oxidation state. An exactly known weight of sample was dissolved in an acid solution (H<sub>2</sub>SO<sub>4</sub>) containing a known amount of sodium oxalate. The excess oxalate was titrated against permanganate. The percentage of manganese obtained by this method was calculated assuming the manganese was in the 4+ oxidation state. The results are: %Mn total = 16.4; %Mn<sup>4+</sup> = 16.5. The nominal manganese content from the Mg<sub>6</sub>MnO<sub>8</sub> formula is 16.7%.

#### X-Ray Analysis.

X-Ray diffraction patterns were obtained by means of a Debye-Scherrer camera, 114.6 mm diameter, using CuK<sub>α</sub> (Ni-filtered) radiation. Table I reports the X-ray diffraction spectrum of the sample.

#### Magnetic measurements.

They were performed using the Gouy method in the temperature range 98–294 K. A Mettler semimicro balance reading to  $\pm 0.01$  mg was

TABLE I  
X-RAY SPECTRUM OF Mg<sub>6</sub>MnO<sub>8</sub>

Our sample		From the literature (9)	
<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub> <sup>a</sup>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>
4.84	s	4.84	60
2.53	m	2.53	15
2.42	w	2.42	11
2.10	vs	2.10	100
1.924	vw	1.923	5
1.613	w	1.613	9
1.483	s	1.482	50
1.417	w	1.417	9
1.278	vw	1.278	1
1.264	w	1.263	9
1.211	m	1.210	16
1.174	vw	1.174	5
1.047	w	1.048	7
0.9612	vw	0.9614	5
0.9371	s	0.9370	26
0.9202	vw	0.9199	3
0.8789	vw	0.8786	3
0.8555	s	0.8554	20
0.8422	vw	0.8423	3
0.8104	vw	0.8102	7
0.8069	vw	0.8065	9
0.7815	vw	0.7815	9

<sup>a</sup> Relative intensities of lines estimated visually: vs = very strong; s = strong; m = medium; w = weak; and vw = very weak.

employed. The instrument was first calibrated with Hg[Co(NCS)<sub>4</sub>]. The molar magnetic susceptibility corrected for the diamagnetism of the sample was found to obey the Curie-Weiss law  $\chi_m = C/(T - \theta)$ . In Table II the values of  $\chi_m$

TABLE II  
MOLAR MAGNETIC SUSCEPTIBILITY  $\chi_m$  AS MEASURED AT DIFFERENT TEMPERATURES

$\chi_m \times 10^3$ (erg · gauss <sup>-2</sup> · mole <sup>-1</sup> )	<i>T</i> (K)
16.7	98
15.8	103
14.5	113
13.5	123
12.8	133
11.9	143
11.3	153
10.7	163
10.1	173
9.6	183
9.1	193
8.7	203
6.2	294

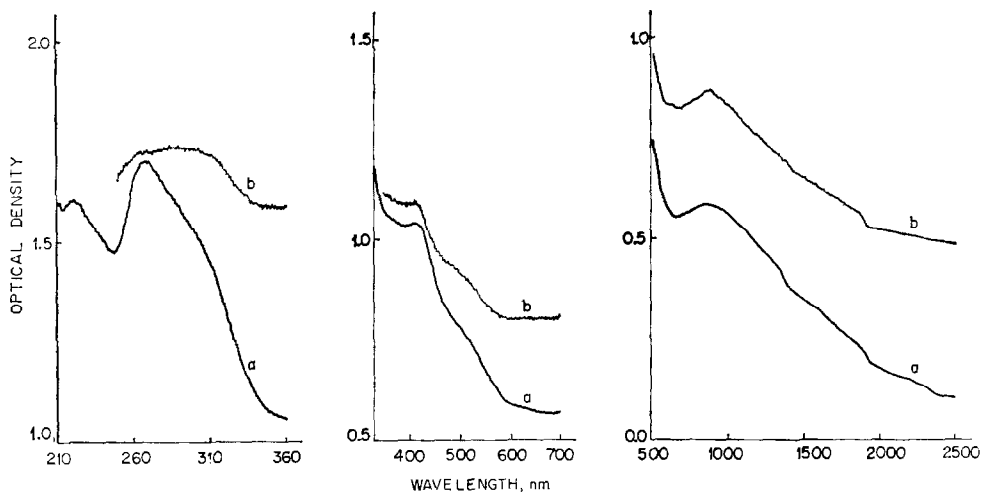


FIG. 2. Reflectance spectrum of  $Mg_6MnO_8$ : (a) at room temperature; (b) at liquid nitrogen temperature.

are reported for each temperature. The Curie constant  $C$  has been obtained from the slope of the  $\chi_m^{-1}$  vs  $T$  plot. The resulting magnetic moment  $\mu$  is field independent and equal to  $3.94 \pm 0.08 \mu_B$  (Bohr magneton), whereas the Weiss temperature  $\theta$  is  $-20 \pm 5$  K.

#### Optical Spectrum

Diffuse reflectance spectra were obtained with a Beckman DK-1 spectrophotometer in the range of 2500–200 nm, both at room and at liquid nitrogen temperature. The specimen was analyzed against MgO as reference. The spectrum is shown in Fig. 2.

#### Results and Discussion

As shown in Table I the powder consists of an uncontaminated  $Mg_6MnO_8$  phase. The results of chemical analyses show that the experimentally determined total manganese content agrees with the value calculated on the basis of the formula  $Mg_6MnO_8$ . Moreover, all the manganese is in the 4+ oxidation state.

The magnetic moment  $\mu$  ( $3.94 \pm 0.08 \mu_B$ ) agrees with the spin-only value expected for a  $d^3$  ion in octahedral configuration ( $3.87 \mu_B$ ); as is well known (12), the spin-orbit contribution is very small in this case. The value of the Weiss temperature  $\theta$  ( $-20 \pm 5$  K) implies a weak anti-ferromagnetic interaction within the solid and is fully consistent with the reported structure of  $Mg_6MnO_8$  (2) in which the  $Mn^{4+}$  paramagnetic ions are far apart [5.9 Å in the (110) direction].

The reflectance spectrum of  $Mg_6MnO_8$  at

room and liquid nitrogen temperature is shown in Fig. 2. All observed bands may be fitted quite satisfactorily on the assumption that the 20.4 kK band represents the first spin-allowed  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition. On the basis of the Tanabe-Sugano diagrams and taking  $10 Dq = 20.4$  kK, the best agreement between experimental and calculated energies is obtained for  $B = 500$  K and  $C = 4.5$  B; being  $B_0 = 1064$  K in gaseous  $Mn^{4+}$  ion (13),  $\beta$  results to be 0.47. The calculated and experimental band positions are reported in Table III together with the probable assignments.

This attribution is in agreement with the results reported by Allen et al. (7) and by Pfeil (8) for  $K_2MnF_6$ . In our case all the bands are shifted towards lower frequencies resulting, as expected from the nature of the bonded anions concerned, in a smaller value of the crystal field parameter  $Dq$ , and a larger covalent bonding in  $Mg_6MnO_8$  with respect to  $K_2MnF_6$  (14).

TABLE III  
EXPERIMENTAL AND CALCULATED BAND POSITIONS (kK)  
FOR  $Mg_6MnO_8$

Band position (kK)		Assignment
Experimental	Calculated	
11.6	10.9	${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}(t_{2g}^3)$
16.0	16.4	$\rightarrow {}^2T_{2g}(t_{2g}^3)$
20.4	20.4	$\rightarrow {}^4T_{2g}(t_{2g}^2 e_g)$
24.4	25.0	$\rightarrow {}^4T_{1g}(t_{2g}^2 e_g)$
33.3		Probably charge transfer
37.8		

The assignment of the 20.4 kK band to the  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition has also been made on the basis of analogy with the spectra of  $\text{Cr}^{3+}$  and  $\text{Mn}^{4+}$  ions dispersed in  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ . In fact the crystal field parameter  $10 Dq$  for  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$  has been found to be 18.2 kK (15), whereas for the same ion in an  $\text{MgO}$  matrix a value of 16.2 kK is reported (16) ( $B = 650$  K in both cases). For the  $\text{Mn}^{4+}$  ion in  $\text{Al}_2\text{O}_3$ ,  $10 Dq$  is 21.3 kK (3). Comparing these data and considering that the structure of  $\text{Mg}_6\text{MnO}_8$  closely resembles the lattice of  $\text{MgO}$  rather than that of  $\text{Al}_2\text{O}_3$ , the value of  $10 Dq$  for  $\text{Mn}^{4+}$  in  $\text{Mg}_6\text{MnO}_8$  should be smaller than 21.3 kK ( $\text{Mn}^{4+}$  in  $\text{Al}_2\text{O}_3$ ). On the other hand, due to the increased charge of  $\text{Mn}^{4+}$  compared to  $\text{Cr}^{3+}$ , the crystal field parameter should be larger for  $\text{Mn}^{4+}$  and thus higher than 16.2 kK ( $\text{Cr}^{3+}$  in  $\text{MgO}$ ). It should be noted that a spectrum similar to that of  $\text{Mg}_6\text{MnO}_8$  (with a broad band centered at about 20.0 kK) has been observed by us for a sample of  $\text{MgO}$  doped with  $\text{Mn}$  and  $\text{Li}$  and containing, as already reported (17),  $\text{Mn}^{4+}$  and  $\text{Li}^+$  ions incorporated in the  $\text{MgO}$  lattice.

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