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A Single Crystal X-Ray Diffraction Study of $\text{Mn}(\text{OH})_2$

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Earlier X-ray studies¹⁻³ have shown $\text{Mn}(\text{OH})_2$ to have the cadmium iodide structure. There is, however, a discrepancy between the Mn—O distance (2.19 Å) obtained by Aminoff,² who studied the mineral pyrochroite by Laue techniques, and that of Natta³ (2.28 Å) from a powder pattern of synthetic $\text{Mn}(\text{OH})_2$. It was therefore decided to redetermine the Mn—O distance in stoichiometric $\text{Mn}(\text{OH})_2$ by a three-dimensional single-crystal X-ray analysis.

Crystals of $\text{Mn}(\text{OH})_2$ were formed by treating 75 ml of a 1.3 m solution of manganese chloride with 100 ml of a 3.7 m solution of lithium hydroxide in a 220 ml pressure bomb lined with pure silver. The balanced pressure technique was used. The average temperature of the pressure bomb was 300°C. The pressure was measured as 650 atm. Thin crystal flakes were formed within 65 h. The pressure bomb was filled and emptied under oxygen free nitrogen, and the crystals of $\text{Mn}(\text{OH})_2$ were washed, dried and stored in an atmosphere of oxygen free nitrogen. The crystals were white and remained so for 6 months.

A plate-shaped crystal of dimensions 0.25 mm × 0.25 mm × 0.01 mm was investigated by precession methods. Integrated precession photographs were taken using Zr-filtered Al-screened $\text{MoK}\alpha$ -radiation of (*hk0*), (*hk1*), (*hk2*) and (*0kl*). 60 independent reflections were measured

Table 1. X-Ray diffraction data for $\text{Mn}(\text{OH})_2$.

$a = 3.322 \pm 0.002 \text{ \AA}, c = 4.734 \pm 0.002 \text{ \AA}$					
<i>d</i> obs	<i>d</i> calc	<i>h</i>	<i>k</i>	<i>l</i>	<i>j</i>
4.750	4.734	0	0	1	50
2.885	2.877	1	0	0	50
2.461	2.458	1	0	1	100
1.828	1.828	1	0	2	25
1.661	1.661	1	1	0	50
1.568	1.567	1	1	1	20
1.375	1.376	2	0	1	20

photometrically. No absorption correction was applied. The unit cell dimensions were determined using a Guinier focussing camera with $\text{CuK}\alpha_1$ radiation and germanium as internal standard. Optical densities of the lines were measured by means of a recording doublebeam microdensitometer. Table 1 gives the indexing of the powder pattern.

The crystal data obtained are: Crystal system: trigonal; using hexagonal setting, the axes are: $a = 3.322 \pm 0.002 \text{ \AA}$, $c = 4.734 \pm 0.002 \text{ \AA}$; space group: No. 164, $P3m$. Absorption coefficient $\mu = 74 \text{ cm}^{-1}$ for $\text{MoK}\alpha$ -radiation. The crystals are tabular on (001).

$\text{Mn}(\text{OH})_2$ is isostructural with $\text{Ca}(\text{OH})_2$.¹ In $\text{Ca}(\text{OH})_2$,⁴ the metal ions are at the centre of symmetry (0,0,0) and the oxygen atoms are in special positions $\pm (1/3, 2/3, 0.2341)$. These coordinates were used when the refinement was started. Coordinates and temperature factors were refined by the method of Bhuiya and Stanley.⁵ The atomic scattering factors used were from Vol. III of *International Tables for X-ray Crystallography*. The interpolation formula of Bassi⁶ was applied. The refinement gave

Table 2. Atomic coordinates and temperature factors.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	σ_z	B (\AA^2)	σB (\AA^2)
Mn	0.0	0.0	0.0		0.48	0.05
O	0.33333	0.66667	0.231	0.003	1.2	0.2

an R -value of 6.5 %. The positions of the hydrogen atoms could not be determined with the present set of data.

Table 2 gives atomic coordinates and temperature factors with their standard deviations. From these coordinates a Mn—O distance of 2.207 Å with a standard deviation of 0.006 Å is calculated. This Mn—O distance is comparable with the Mn—O distance 2.22 Å, which is calculated from the unit cell parameter 4.445 Å reported for MnO.⁷ A radius of 0.68 Å is calculated for the Mn²⁺ ion using the value of 1.53 Å for the ionic radius of OH⁻, and a radius of 0.82 Å is obtained when using the value of 1.40 Å for O²⁻ (Pauling). Apparently the concept of ionic radius for Mn²⁺ is inadequate. From an investigation of magnetic scattering of neutrons in MnO the radial distribution of the electrons in the 3d-shell of the Mn²⁺ ion was calculated by Shull, Strauser and Wollan⁸ and a maximum of the electron radial density was found in the vicinity of radius 0.6 Å.

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On the Structure of the Spinel CuMn₂O₄

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Most spinels AB_2O_4 , where A represents a divalent ion and B manganese ions, are tetragonal because of the distorting tendency showed by octahedrally coordinated Mn³⁺ ions. CuMn₂O₄, which is of the above mentioned type if Cu is supposed to be divalent has, however, $c/a = 1$. Dunitz and Orgel¹ have advanced the hypothesis that this should be due to the cooperating effect of the two Jahn-Teller ions, Cu²⁺ and Mn³⁺, which according to an X-ray powder investigation by Sinha *et al.*² are distributed so as to give a normal spinel. The inversion parameter λ , as defined by the formula $[\text{Mn}\lambda\text{Cu}_{1-\lambda}]_{\text{tet}}[\text{Cu}\lambda\text{Mn}_{2-\lambda}]_{\text{oct}}\text{O}_4$ is thus equal to 0. According to those authors this value is independent of temperature. The oxygen positional parameter was determined by trial and error methods as $u = 0.267$ (or 0.392, if another origin is chosen).

The result of an X-ray powder study by Zaslavskii *et al.*³ shows, however, that CuMn₂O₄ is not a normal spinel but partially inverted, with the inversion parameter λ within the limits $0.67 \leq \lambda \leq 1$. A more precise determination of λ was considered impossible "in view of the considerable superposition of reflections and the similarity in scattering factor of the copper and manganese atoms". The oxygen parameter u was assumed to have the ideal value of 0.250 (0.375).

A further value of the inversion parameter λ has been reported by Delorme⁴ who derived $\lambda = 0.34$ from the ratio of the intensities of the two powder reflections 400 and 422. This value was found to be independent of temperature.

The results obtained by Larson *et al.*⁵ from electrical conductivity and magnetic data on NiMn₂O₄, which indicate that manganese is partially present as Mn²⁺ and Mn⁴⁺, suggest that this may also be the case in CuMn₂O₄. From this point of view a detailed structural study of CuMn₂O₄ was considered desirable and was undertaken within a research program