

Preparation and Magnetic Properties of Manganite*

W. S. GLAUNSINGER†

Department of Chemistry, Arizona State University, Tempe, Arizona 85281

H. S. HOROWITZ AND J. M. LONGO

Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

Received May 24, 1978; in final form September 15, 1978

A new hydrothermal synthesis of manganite is described, and the magnetic and electron paramagnetic resonance (EPR) behavior of the product is reported. The magnetic susceptibility is nearly independent of temperature above 90°K and increases dramatically on cooling to 30°K. The EPR lineshape, linewidth, and g-factor at 296°K are Lorentzian (in the central region), 280 ± 10 G, and 1.997 ± 0.006 , respectively. The EPR spectrum is interpreted in terms of nearly one-dimensional interactions between identical Mn moments. The results of this study support the view that all Mn ions are trivalent and that the magnetic interactions between these ions are nearly one dimensional.

Poorly crystallized manganese oxides of the type $\text{Mn}_x^{3+} \text{Mn}_{1-x}^{4+} \text{O}_{2-x} (\text{OH})_x$ are of considerable importance in the battery industry. Among these oxides, the mineral manganite ($\gamma\text{-MnOOH}$) has a well-defined existence, and its structure has been investigated by X-ray (1) and neutron diffraction (2). Manganite crystallizes in a monoclinic, slightly deformed Markasite (FeS_2) structure and has unit-cell dimensions $a = 8.88 \text{ \AA}$, $b = 5.25 \text{ \AA}$, $c = 5.71 \text{ \AA}$, and $\beta = 90^\circ$. There are eight Mn ions per cell, with each Mn ion being at the center of an octahedron formed by three oxygens and three hydroxyl groups. The Mn ions are crystallographically equivalent and form a nearly body-centered orthorhombic lattice. Single-crystal neutron studies have indicated that $\gamma\text{-MnOOH}$

orders antiferromagnetically at $45 \pm 3^\circ\text{K}$ and has a magnetic helical structure with a pitch of 4.92 \AA at 4.2°K (3). Since two oxygen atoms separate manganese neighbors in the a and b directions, the exchange interactions between Mn ions in these directions should be weak. From the pitch of the magnetic helix, it was estimated that the Mn-Mn interaction in the chain extending in the c direction is four times as large as that between chains (3), so that the magnetic interactions in manganite are of low dimensionality.

Reports in the literature about thermally prepared manganite involve some measure of doubt concerning the identification of the final product (4, 5). Furthermore, both X-ray (1) and neutron (2, 3) analysis indicate that all the Mn ions are trivalent, whereas magnetic anisotropy measurements suggest that the mean Mn valency of 3 is achieved by equal numbers of divalent and tetravalent

* This research was supported in part by a Faculty Research Participation Fellowship (W.S.G.) and Grant DMR 75-09215 from the National Science Foundation.

† To whom inquiries should be addressed.

ions (6). In this paper we describe a new hydrothermal synthesis of manganite and report the magnetic and electron paramagnetic resonance (EPR) behavior of the product.

Manganite was prepared by dispersing 0.5 g of γ -MnOOH, prepared by the method of Feitknecht and Marti (4), into about 0.05 liter of a 0.1 N RbOH solution. The solution was transferred into a conventional autoclave and sufficient H_2SO_4 was added to make the pH of the solution 7.5–8.5. The autoclave was flushed with oxygen, sealed, and heated at a rate of 50°C/h to the reaction temperature of 250°C. After 3 days the autoclave was air-quenched to ambient temperature, and the precipitate was filtered, washed with distilled water, and dried at about 60°C in a vacuum oven. The positions of the X-ray diffraction lines of the dried precipitate were identical to those of natural manganite, and the narrowness of these lines indicated that the product was well crystallized. In contrast, the diffraction lines of the starting material were very broad and difficult to identify.

The magnetic susceptibility of the precipitate was measured in the range 4.2–300°K using a Faraday apparatus described elsewhere (7). The setup was calibrated with Pt and HgCo (SCN)₄, and the susceptibility was measured at five magnetic fields ranging from 2.5 to 13 kG. The susceptibility was independent of field above about 48°K, but below this temperature it decreased by over a factor of 2 in going from 2.5 to 13 kG. This type of field-dependent behavior is characteristic of weak ferromagnetism. Since the susceptibility vs reciprocal field was linear below 48°K, extrapolation of the susceptibility to infinite field should eliminate the ferromagnetic behavior. The temperature dependence of the resulting molar susceptibility is shown in Fig. 1. Above 77°K the susceptibility is in reasonable agreement with two previous studies (3, 5), but the large increase in susceptibility on cooling to 30°K is not observed in natural manganite. However, in both previous studies there was no indication that the susceptibility was measured as a function of field. The nearly temperature-independent susceptibility

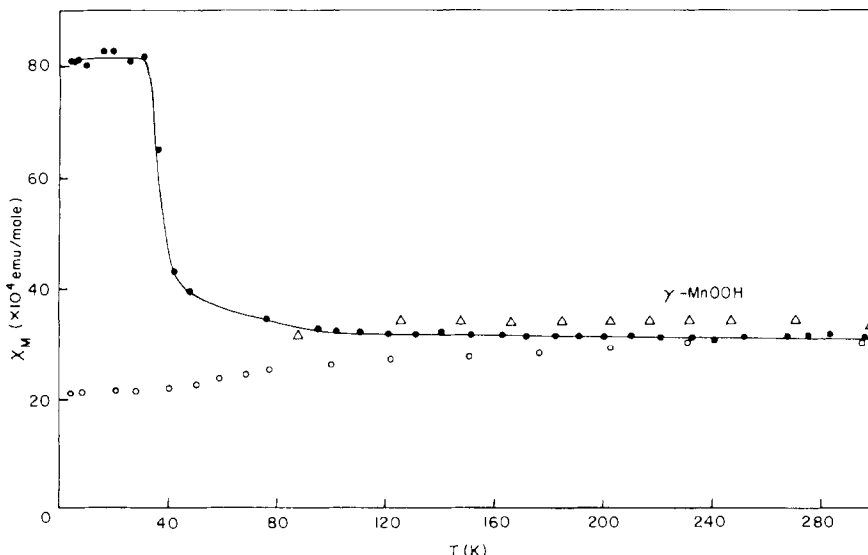


FIG. 1. Temperature dependence of the magnetic susceptibility of manganite. Solid dots, open dots and triangles are for hydrothermally prepared (this work), naturally occurring (3), and thermally prepared (5) manganite, respectively.

above 90°K is characteristic of one-dimensional magnetic chains (8). The field dependence and the increase with decreasing temperature of the susceptibility begin near the Néel temperature T_N , which suggests that the weak ferromagnetism is perhaps associated with the antiferromagnetic ordering of the Mn moments. The poor agreement between the susceptibilities of hydrothermally prepared and naturally occurring manganite may indicate that the Honda-Owen extrapolation below 48°K may not yield accurate susceptibilities.

EPR spectra of synthetic manganite were recorded at 296°K using a Varian E-12 spectrometer. g -factors were determined using pitch in KCl as an internal standard. A typical EPR spectrum is shown in Fig. 2. Mn^{2+} was not detected, even at the highest spectrometer sensitivities. The lineshape is Lorentzian in the central region, the peak-to-peak linewidth is 280 ± 10 G, and the g -factor is 1.997 ± 0.006 . The Lorentzian lineshape is typical of exchange-coupled localized moments (9), and for a linear-chain

system implies weak interchain coupling producing a three-dimensional ordering below some critical temperature (10). Since the calculated dipolar width is about 5 kG, the narrow line observed indicates that the exchange narrowing is extreme. The linewidth for one-dimensional exchange narrowing is given by

$$\Delta H \sim M_2^2/H_e, \quad (1)$$

where M^2 is the second moment and H_e is the exchange field (10). Taking $\Delta H \sim 0.3$ kG and $M_2 \sim 5$ kG², we find $H_e \sim 9 \times 10^5$ G. Hence we predict $T_N < 120^\circ\text{K}$, which is found experimentally. Moreover, we expect the EPR line to broaden dramatically as T_N is approached due to the increasing frequency of critical fluctuations near the ordering temperature. The extreme exchange narrowing of the EPR line at 296°K shows that the Mn moments are identical (11), and the proximity of the g -factor to its spin-only value precludes any appreciable orbital contribution to the Mn moment. We emphasize that spin-only moments have

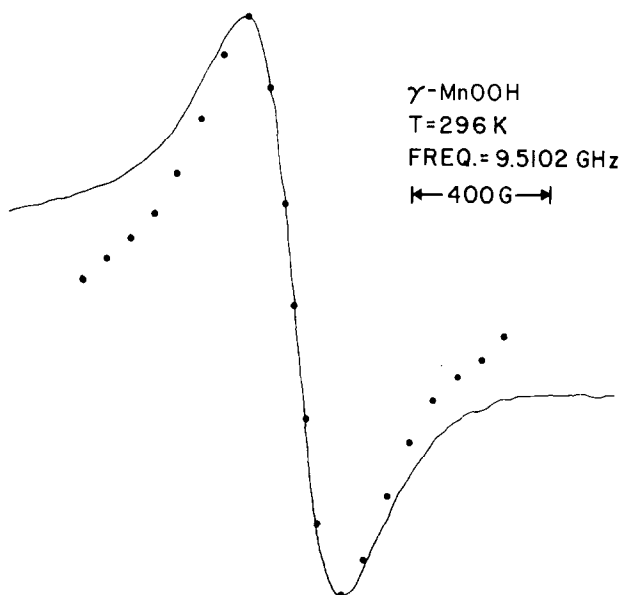


FIG. 2. EPR spectrum of hydrothermally prepared manganite at 296°K. The dots are values computed from a Lorentzian lineshape function.

been observed in other compounds containing Mn^{3+} octahedrally coordinated by six oxygens (12, 13), and the occurrence of such moments have been explained theoretically by Van Vleck (14) and Siegert (15). Hence, in agreement with neutron-diffraction work (3), our results support the view that all the Mn ions are trivalent and that the magnetic interactions between these ions are nearly one dimensional.

Acknowledgments

We wish to thank Mr. Harold Brady for assistance in sample preparation and Professor M. J. Sienko for the use of his laboratory for the magnetic susceptibility measurements.

References

1. M. J. BUERGER, *Z. Kristallogr.* **95**, 163 (1936).
2. H. DACHS, *Z. Kristallogr.* **118**, 303 (1963).
3. H. DACHS, *Int. J. Magn.* **4**, 5 (1973).
4. W. FEITKNECHT AND W. MARTI, *Helv. Chim. Acta* **28**, 149 (1945).
5. T. E. MOORE, M. ELLIS, AND P. W. SELWOOD, *J. Amer. Chem. Soc.* **72**, 856 (1950).
6. K. S. KRISHNAN AND S. BANNERJEE, *Trans. Faraday Soc.* **35**, 385 (1939).
7. J. E. YOUNG, Jr., Ph.D. Thesis, Cornell University, 1970.
8. J. C. BONNER AND M. E. FISHER, *Phys. Rev.* **135**, A640 (1964).
9. W. S. GLAUNSINGER, *J. Magn. Res.* **18**, 265 (1975).
10. M. J. HENNESSY AND C. D. McELVEE, *Phys. Rev. B* **7**, (1973).
11. C. P. SLICHTER, "Principles of Magnetic Resonance" (F. Feitz, Ed.), p. 112, Harper and Row, New York (1963).
12. S. S. BHATNAGAR, P. L. KAPUR, AND B. PRAKASH, *Curr. Sci.* **8**, 253 (1939).
13. G. H. JONKER AND J. H. VAN SANTEN, *Physica* **16**, 337 (1950).
14. J. H. VAN VLECK, *Phys. Rev.* **41**, 208 (1932).
15. A. SIEGERT, *Physica* **3**, 85 (1936); **4**, 138 (1937).