

Bidimensional Magnetic Properties of β - Sr_2MnO_4

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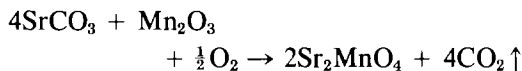
β - Sr_2MnO_4 belongs to the K_2NiF_4 -type structure. The magnetic structure studied by neutron diffraction is characterized by antiferromagnetic interactions between nearest-neighbor Mn^{4+} ions. The value of the exchange integral J/k calculated by the high-temperature series expansion method is about -80 K. All magnetic properties of β - Sr_2MnO_4 show the 2D character of the magnetic interactions and illustrate the strong covalency of the Mn-O bonds within the magnetic layers.

In the scope of a general study of the magnetic properties of layer oxides, we discuss here the results obtained for β - Sr_2MnO_4 which has a K_2NiF_4 -type structure.

Sr_2MnO_4 was first prepared by Baltz and Plieth. The phase obtained was identified as isostructural with K_2NiF_4 ; the cell parameters were: $a = 3.79$ Å and $c = 12.43$ Å (1). In a previous study of the strontium-manganese-oxygen system, Mizutani *et al.* (2) have shown that Sr_2MnO_4 exists actually with two allotropic forms: a low-temperature α variety of undetermined structure and the high-temperature β form, with the K_2NiF_4 -type structure, whose cell parameters are close to those determined previously: $a = 3.787$ Å and $c = 12.495$ Å. The $\alpha \rightarrow \beta$ transformation takes place between 1500 and 1600°C. The high-temperature β form can be obtained by quenching to room temperature, the reverse $\beta \rightarrow \alpha$ transformation occurs only when the sample is annealed for at least 8 hr at 1200°C.

I. Preparation

β - Sr_2MnO_4 has been obtained by heating α - Sr_2MnO_4 in air at 1650°C for 30 min, the latter being prepared upon calcination in an oxygen stream of a mixture of SrCO_3 and Mn_2O_3 according to



Two successive heating treatments, one of 15 hr at 900°C and the other of 15 hr at 1200°C were necessary to obtain a pure α phase.

The cell parameters of the β phase, $a = 3.787$ Å and $c = 12.496$ Å, are very close to those announced before (2). The X-ray diffraction spectrum confirms that β - Sr_2MnO_4 is isostructural with K_2NiF_4 . The observation of systematic extinctions corresponding to $h + k + l = 2n + 1$ agrees with space group $I4/mmm$, typical of tetragonal K_2NiF_4 -type phases.

Due to the preparation method it may be supposed that β - Sr_2MnO_4 contains a certain number of Mn^{3+} ions which, although small, is not negligible. As shown previ-

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ously, the presence of some Mn³⁺ ions in such a material leads to a sharp increase in electronic conductivity and conversely a rapid decrease in the activation energy for conduction (3).

Conductivity measurements on β -Sr₂MnO₄ have been carried out between 300 and 700 K for polycrystalline samples. The variation of $\log \sigma$ with reciprocal temperature is given in Fig. 1. The results are similar to those previously obtained for Ca₂MnO₄. A small conductivity and a high activation energy for conduction are observed ($\Delta E = 0.39$ eV), suggesting thus that the presence of relatively few Mn³⁺ ions in the samples.

Susceptibility measurements are consistent with this result. The variation of magnetization with applied field suggests that there is no ferromagnetic component in the sample at low temperature, and thus no significant Mn³⁺-Mn⁴⁺ coupling.

II. Neutron Diffraction Study

The neutron diffraction patterns have been obtained with the high-resolution diffractometer D_{10} of the Laüe-Langevin Institute using wavelength $\lambda = 2.52$ Å. Filters of pyrolytic graphite were put into the incident beam to avoid second- and third-harmonic contaminations. Powders were

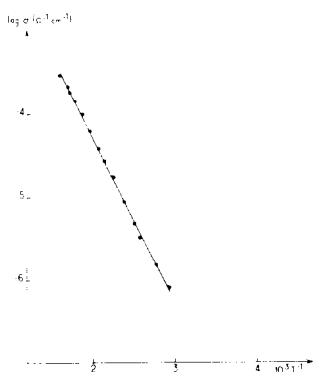


FIG. 1. Variation of β -Sr₂MnO₄ conductivity with temperature ($\Delta E = 0.39$ eV).

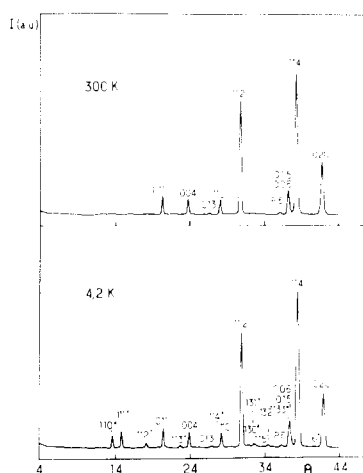


FIG. 2. Neutron diffraction patterns of β -Sr₂MnO₄ at 4.2 and 300 K (x indicates magnetic line positions).

placed in a vanadium holder whose contribution at $\theta = 36^\circ$ is indicated in the patterns.

1. Crystallographic Structure Determination

This study has been made in order to determine the atomic positions in the unit cell, particularly those of oxygen. The Fermi lengths used were

$$\begin{aligned} b_{\text{Sr}} &= 0.69 \cdot 10^{-12} \text{ cm}, \\ b_{\text{Mn}} &= -0.37 \cdot 10^{-12} \text{ cm}, \text{ and} \\ b_{\text{O}} &= 0.597 \cdot 10^{-12} \text{ cm}. \end{aligned} \quad (4)$$

The patterns have been obtained at 300 and 4.2 K, peaks representing magnetic contribution are not taken into account for the last temperature (Fig. 2). The calculations were carried out on the basis of the atomic positions in a K₂NiF₄ structure with $I4/mmm$ space group.

A reliability factor $R = 0.02$ was obtained with atomic positions given as in Table I.

The β -Sr₂MnO₄ structure consists of a stacking of two-dimensional layers, perpendicular to the c axis, these layers being built up of [MnO₆] octahedra sharing common corners with four surrounding octahedra.

TABLE I
REDUCED ATOMIC COORDINATES IN THE β - Sr_2MnO_4
STRUCTURE

	Site	x	y	z
Sr	$4e$	0	0	0.356 (4.2 K) 0.356 (300 K)
Mn	$2a$	0	0	0
O_I	$4c$	0	$\frac{1}{2}$	0
O_{II}	$4e$	0	0	0.157 (4.2 K) 0.157 (300 K)

The rigidity of the lattice is maintained by Sr^{2+} ions which occupy 9-coordinate sites.

At 300 K the Mn– O_I distance in the equatorial planes is equal to 1.894 Å, which is slightly smaller than both the sum of the ionic radii for Mn^{4+} and O^{2-} ions (1.930 Å) as proposed by Shannon and Prewitt (5) and the Mn–O distance of 1.903 Å observed in the β - SrMnO_3 perovskite-type structure (2). Along the c axis, the Mn– O_{II} axial distance is 1.976 Å which suggests that the MnO_6 octahedra are only slightly distorted: $(\text{Mn}-\text{O}_{ax})/(\text{Mn}-\text{O}_{eq}) = 1.04$.

The Sr–O distances are respectively $4[\text{Sr}-\text{O}_I = 2.610 \text{ \AA}]$, $4[\text{Sr}-\text{O}_{II} = 2.677 \text{ \AA}]$, and $\text{Sr}-\text{O}_{II} = 2.485 \text{ \AA}$, giving an average Sr–O of 2.626 Å, which is intermediate between the Sr–O distance in SrO (2.58 Å) (6) and in β - SrMnO_3 (2.691 Å) (2).

2. Magnetic Structure Determination

The patterns obtained below the ordering temperature ($T_N = 170 \text{ K}$) show additional reflections whose nature is purely magnetic (Fig. 2).

The magnetic and crystallographic cells are related as follows:

$$a_{\text{magn}} = 2a_{\text{cryst}},$$

$$c_{\text{magn}} = c_{\text{cryst}}.$$

Two propagation vectors are possible: $\mathbf{k}_1 = [\frac{1}{2}, \frac{1}{2}, 0]$ and $\mathbf{k}_2 = [-\frac{1}{2}, \frac{1}{2}, 0]$. If \mathbf{S}_1 and \mathbf{S}_2 are the magnetic moments of Mn^{4+} ions at (000) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the nuclear cell, it is possible to define two linear combinations

TABLE II

Symmetrical irreducible representation of the $Immm$ group	$\mathbf{k}_1 = [\frac{1}{2}, \frac{1}{2}, 0]$	$\mathbf{k}_2 = [-\frac{1}{2}, \frac{1}{2}, 0]$
	Γ_g^1	—
Γ_g^2	A_z	F_z
Γ_g^3	$A_x + A_y$	$F_x - F_y$
Γ_g^4	$A_x - A_y$	$F_x + F_y$

of \mathbf{S}_1 and \mathbf{S}_2 , $\mathbf{F} = \mathbf{S}_1 + \mathbf{S}_2$ and $\mathbf{A} = \mathbf{S}_1 - \mathbf{S}_2$, which characterize respectively the ferro- and antiferromagnetic modes. Research of the base vectors in the irreducible representation of the $Immm$ space group gives the modes reported in Table II.

The comparison between calculated and observed intensities shows that the magnetic structure can be described on the base of the strictly identical modes Γ_g^2 , A_z , or F_z (Table III). The structure refinement at 4.2 K ($R = 0.027$) gives a magnetic moment of $2.42 \pm 0.05 \mu_B$ for the Mn^{4+} ions.

From the temperature dependence of the magnetic moment, shown in Fig. 3, it is possible to estimate the Néel temperature at $T_N = 170 \pm 5 \text{ K}$.

The magnetic structure of β - Sr_2MnO_4 is given in Fig. 4 and is similar to that of K_2NiF_4 . The magnetic moments of Mn^{4+} are parallel to the c axis. In the $[\text{MnO}_4]_n$ layers, each Mn^{4+} ion is surrounded by four neighbours of opposite spin. An identical layer can be obtained by a $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ translation. Similar magnetic layer lie in the c direction with a period equal to c . As a consequence, the structure is different from that of

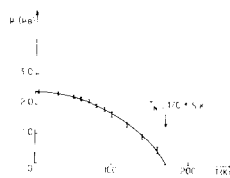
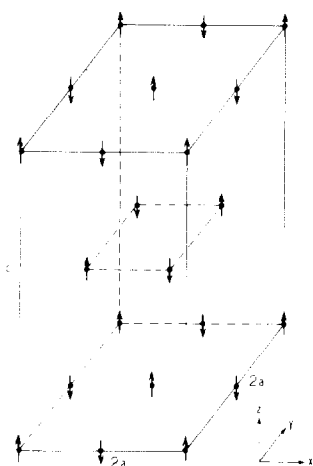


FIG. 3. Variation of magnetic moment of β - Sr_2MnO_4 with temperature.

FIG. 4. Magnetic structure of β - Sr_2MnO_4 .

Ca_2MnO_4 where the magnetic period is $2c$ (8).

III. Calculation of the Exchange Integral

The measurements of magnetic susceptibility have been carried out under helium in either a Faraday-type balance or a Foner-type magnetometer at temperatures between 4 and 1000 K.

Experimental values have been corrected from the diamagnetic contributions and the second-order Zeeman effect for Mn^{4+} ions. The spin-orbital coupling constant used was 138 cm^{-1} (9), the octahedral ligand-field splitting was $22,000 \text{ cm}^{-1}$ (10).

The thermal dependence of the recipro-

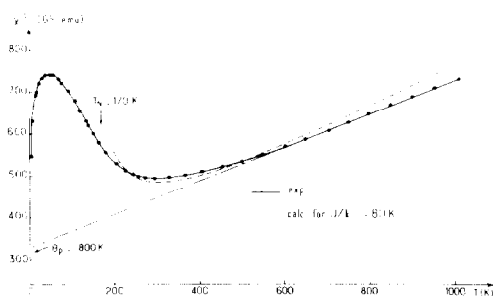


FIG. 5. Thermal variation of reciprocal molar susceptibility of β - Sr_2MnO_4 .

cal molar susceptibility is given in Fig. 5. At low temperature the paramagnetic impurities—eventually isolated Mn^{3+} ions—give rise to the decrease of χ^{-1} . The curve shows an extended minimum between 200 and 400 K. At high temperature the curve becomes progressively linear: this behavior is characteristic for lower-dimensional magnetic couplings which is probably 2D, due to the structural features.

The Curie constant calculated from susceptibility measurements at high temperature is 2.1. This value is larger than the spin-only value, $C_{\text{calc}} = 1.875$, expected for a spin $\frac{3}{2}$. The paramagnetic Curie temperature is estimated to be $-800 \pm 10 \text{ K}$.

The exchange integral has been estimated by the high-temperature series expansion method. We have used the Rushbrooke and Wood equations for the case of a square model with $S = \frac{3}{2}$ where Heisenberg interactions persist (11). From the experimental susceptibility values the J/k integral obtained is approximately -80 K .

IV. Discussion of the Results

The magnetic properties of β - Sr_2MnO_4 have been compared with those of its iso-

TABLE III
OBSERVED AND CALCULATED
MAGNETIC INTENSITIES WITH THE
 A_2 MODE

$h k l$	I_{obs}	I_{calc}^a
1 1 0	10.7	11.06
1 1 1	18.1	17.93
1 1 2	10.8	10.83
1 1 3	5.8	5.88
1 1 4	—	3.01
1 3 0	10.8	9.70
1 3 1	25.8	18.10
1 1 5	—	1.6
1 3 2	14.1	14.7

^a The form factor for Mn^{4+} ions is that used by Watson and Freeman (7).

TABLE IV
COMPARISON WITH SOME MAGNETIC DATA FOR
CALCIUM AND STRONTIUM OXIDES

	Mn-Mn (Å)	T_N (K)	J/k (K)	μ (μ_B)	Reference
CaMnO ₃	3.73	130	-24	2.64(4.2 K)	(12-14)
β -SrMnO ₃	3.805	260	-48	2.6(77 K)	(15)
Ca ₂ MnO ₄	3.667	115	-52	2(4.2 K)	(8, 12, 16)
β -Sr ₂ MnO ₄	3.787	170	-80	2.42(4.2 K)	This study

type Ca₂MnO₄ in Table IV. Additionally, results for CaMnO₃ and the perovskite-like β -SrMnO₃ are given to show the influence of dimensionality on the properties of β -Sr₂MnO₄. The values of the ordering temperatures are those determined by neutron diffraction and the exchange integrals are calculated on the basis of Rushbrooke and Wood equations.

From a structural point of view, the distances between magnetic ions always decrease from the perovskite-type to the K₂NiF₄ phase. However, this difference is less important for the strontium than for the calcium compounds.

The value of J/k for β -Sr₂MnO₄ characterizes strong magnetic interactions between neighbor Mn⁴⁺ ions, the antiferromagnetic coupling being due to half-filled t_{2g} orbitals. This value is appreciably lower than that observed for the homologous perovskite-like β -SrMnO₃ (-48 K). Such an evolution is always observed in oxides of K₂NiF₄ structure (17).

In the magnetic structure of β -Sr₂MnO₄, there is no field created around a magnetic ion by the eight nearest-neighbor Mn⁴⁺ ions in the (001) adjacent planes (Fig. 4). This suggests that magnetic interactions between close layers of Mn⁴⁺ ions are small. In agreement with the resulting bidimensional character of the couplings, the ordering temperature ($T_N = 170$ K) is slightly larger than the Stanley-Kaplan temperature calculated for β -Sr₂MnO₄ ($T_{SK} = 156$ K) (18, 19).

At 4.2 K the value of the magnetic mo-

ment for the Mn⁴⁺ ion, 2.42 μ_B , is much smaller than that expected for a 3d³ ion: as the system is bidimensional this difference is probably due to the zero-point spin deviation effect and the strong covalent character of the Mn⁴⁺-O bond in the magnetic layers.

Table IV shows that the substitution of calcium by strontium leads to an increase of ordering temperature (from 115 K (8) to 170 K) and of the strength of magnetic couplings (J/k goes from -52 K (16) to -80 K) despite greater Mn-Mn distances within the layers. A similar evolution has been observed for the Ca_{1-x}Sr_xMnO₃ perovskite-type solid solution where $dT_N/da > 0$, a being the unit cell parameter (20, 21). As Goodenough has pointed out in this case, the π (Mn-O) and σ (Ca, Sr-O) bonds are in competition: the progressive substitution of calcium by more basic strontium induces increasing covalency of the Mn-O bonds. This effect prevails on the influence of rising Mn-Mn distances due to bigger size of the alkaline earth. A quite similar analysis can be applied to the Ca₂MnO₄ and β -Sr₂MnO₄ phases.

This study of the magnetic properties of β -Sr₂MnO₄ does indeed emphasize both the 2D character of the magnetic interactions between neighboring Mn⁴⁺ ions and the strong covalency of the Mn-O bonding within the magnetic layers.

References

1. D. BALTZ AND K. PLIETH, *Z. Electrochem.* **59**, 545 (1955).
2. N. MIZUTANI, A. KITAZAWA, N. ONKUMA, AND M. KATO, *Kogyo Kagaku Zasshi* **43**(6), 1097 (1970).
3. C. CHAUMONT, A. DAUDI, G. LE FLEM, AND P. HAGENMULLER, *J. Solid State Chem.* **14**, 335 (1975).
4. G. E. BACON, *Neutron Diffraction Newsletters*, 1978.
5. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. Sect. B* **25**, 925 (1969); **26**, 1046 (1970).

6. H. E. SWANSON, N. T. GILFRICH, AND G. M. UGRINIC, *Nat. Bur. Stand. Circ.* **539**, 75 (1955).
7. R. E. WATSON AND A. J. FREEMAN, *Acta Crystallogr.* **14**, 27 (1961).
8. D. E. COX, G. SHIRANE, R. J. BIRGENEAU, AND J. B. MACCHESNEY, *Phys. Rev.* **188**(2), 930 (1969).
9. F. E. MABBS AND D. J. MACHIN, Eds. "Magnetism in Transition Metal Complexes" Chapman & Hall, London (1973).
10. A. LOUAT, Doctorat és Sciences thesis, University of Lyon (1968).
11. G. S. RUSHBROOKE AND P. J. WOOD, *Mol. Phys.* **1**, 257 (1958).
12. J. B. MACCHESNEY, N. J. WILLIAMS, J. F. POTTER, AND R. C. SHERWOOD, *Phys. Rev.* **164**, 779 (1967).
13. E. O. WOLLAN AND W. C. KOEHLER, *Phys. Rev.* **100**, 545 (1955).
14. V. M. YUDIN, A. I. GAVRILISHIMA, M. V. ARTEM'eva, AND M. F. BRYZKINA, *Fiz. Tverd. Tela* **7**, 2292 (1965).
15. T. TAKEDA AND S. OHARA, *J. Phys. Soc. Japan* **37**, 275 (1974).
16. M. E. LINES, *J. Phys. Chem. Solids* **31**, 101 (1970).
17. J. L. SOUBEYROUX, PH. COURBIN, L. FOURNES, D. FRUCHART, AND G. LE FLEM, *J. Solid State Chem.* **31**(3), 313 (1980).
18. H. E. STANLEY AND T. A. KAPLAN, *Phys. Rev. Lett.* **17**, 913 (1966).
19. L. J. DE JONGH AND A. R. MEDIEMA, *Adv. Phys.* **23**, 1 (1974).
20. J. B. GOODENOUGH, *Phys. Rev.* **164**(2), 785 (1967).
21. J. F. KAFALAS, N. MENYUK, K. DWIGHT, AND J. M. LONGO, *J. Appl. Phys.* **42**(4), 1497 (1971).