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Neutron-Diffraction Study of Magnetic Ordering in  $\text{Ca}_2\text{MnO}_4$ †

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$\text{Ca}_2\text{MnO}_4$  shows anomalous magnetic-susceptibility behavior rather similar to that of the isostructural fluoride  $\text{K}_2\text{NiF}_4$ , in which the existence of long-range two-dimensional character has recently been clearly demonstrated. A powder-diffraction study of  $\text{Ca}_2\text{MnO}_4$  with 2.5 Å neutrons has revealed that three-dimensional ordering sets in at about 114°K with an antiferromagnetic structure different from that of  $\text{K}_2\text{NiF}_4$ . The antiferromagnetic basal-plane arrangement of the latter is retained, but the layers are stacked in such a way that adjacent *c*-axis moments 12 Å apart are coupled antiparallel instead of parallel, and the magnetic unit cell is double the chemical cell in this direction. The moments are directed along [001] and their magnitude is  $2.0 \mu_B$  per  $\text{Mn}^{4+}$  ion, significantly less than the spin-only value of  $3 \mu_B$ . Above 114°K, there are indications of two-dimensional effects, but these are not so pronounced as in  $\text{K}_2\text{NiF}_4$ .

## I. INTRODUCTION AND EXPERIMENTAL DETAILS

THERE has recently been a considerable amount of theoretical interest in two-dimensional magnetic systems,<sup>1</sup> which are predicted to differ in a number of important respects from three-dimensional systems. The most extensively studied example to date is the tetragonal compound  $\text{K}_2\text{NiF}_4$ , which exhibits unusual susceptibility behavior<sup>2</sup> and has been studied in some detail by Plumier<sup>3</sup> using powder-neutron-diffraction techniques. His results led him to postulate a model in which there was strong antiferromagnetic coupling between nearest neighbors within the basal planes below about 180°K, with extensive stacking faults in the order between the planes, even as low as 4.2°K. However, the real nature of the magnetic scattering has only recently been revealed in a single-crystal neutron study, in which long-range two-dimensional character was found to be present between 97.2 and 200°K.<sup>4</sup> There is a sharp

transition at 97.1°K, below which the crystal becomes ordered three dimensionally. This picture is also consistent with the susceptibility data,<sup>2</sup> which show a broad maximum around 250°K and a sharp minimum in the perpendicular component slightly below 100°K.

Recently, magnetic measurements have been made on a number of calcium manganese oxides,<sup>5</sup> including  $\text{Ca}_2\text{MnO}_4$ , which is isostructural with  $\text{K}_2\text{NiF}_4$  and also shows unusual susceptibility behavior, with a very shallow maximum around 220°K and a fairly sharp peak at 114°K. This has been interpreted in terms of a two-dimensional model by Lines.<sup>6</sup>

The present paper describes a neutron-diffraction investigation of  $\text{Ca}_2\text{MnO}_4$  which has revealed rather unexpectedly that the magnetic structure of  $\text{Ca}_2\text{MnO}_4$  is not the same as that of  $\text{K}_2\text{NiF}_4$ , and that although there are indications of two-dimensional character, this is not present to the same degree as in the latter compound.

The sample of  $\text{Ca}_2\text{MnO}_4$  was prepared by the same means used to synthesize the material for the magnetic study.<sup>5</sup> Powder of the correct Ca:Mn ratio was first fired in air at 1350°C and then annealed under a pressure of 17 000 psi of oxygen at 740°C. This procedure

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<sup>1</sup> For a comprehensive survey see M. E. Lines, *J. Appl. Phys.* **40**, 1352 (1969).

<sup>2</sup> K. G. Srivastava, *Phys. Letters* **4**, 55 (1963).

<sup>3</sup> R. Plumier, *J. Phys. Radium* **24**, 741 (1963); *J. Appl. Phys.* **35**, 950 (1964); E. Legrand and R. Plumier, *Phys. Status Solidi* **2**, 317 (1962); R. Plumier and E. Legrand, *J. Phys. Radium* **23**, 474 (1962).

<sup>4</sup> R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, *Phys. Rev. Letters* **22**, 720 (1969).

<sup>5</sup> J. B. MacChesney, H. J. Williams, J. F. Potter, and R. C. Sherwood, *Phys. Rev.* **164**, 779 (1967).

<sup>6</sup> M. E. Lines, *Phys. Rev.* **164**, 736 (1967); also (private communication).

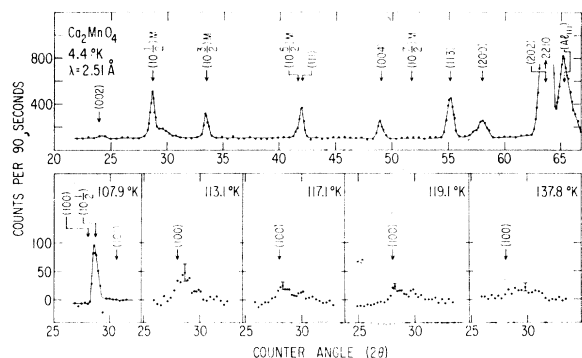


FIG. 1. Top: neutron-diffraction pattern from  $\text{Ca}_2\text{MnO}_4$  at 4.4°K. All peaks indexed on a unit cell with  $a = a_0\sqrt{2}$ ,  $c = c_0$  in terms of chemical cell. Bottom: difference patterns  $I(T^\circ\text{K}) - I(200^\circ\text{K})$  at various temperatures. Vertical bars denote standard deviations of counting statistics.

yielded a specimen having 99.6% of the Mn as the tetravalent ion. The sample was polycrystalline, since this sort of synthesis does not enable single crystals to be obtained very readily. Although the x-ray pattern of the material was single-phase ( $a = 3.667 \text{ \AA}$ ,  $c = 12.06 \text{ \AA}$ ), a preliminary neutron-diffraction run showed a small impurity peak which could not be positively identified, but may possibly result from  $\text{Ca}_3\text{Mn}_2\text{O}_7$ .

## II. DATA COLLECTION AND STRUCTURE ANALYSIS

In order to obtain high resolution of the low-angle magnetic peaks, relatively long-wavelength neutrons from a Ge monochromator in the (111) position were used. The optimum wavelength is about 2.5 Å, since third-order contamination can be reduced to a negligible level with a "filter" of pyrolytic graphite 2 in. in thickness with relatively little attenuation of the main beam.<sup>7</sup>

Data were collected initially at 200 and 4.4°K. The former did not reveal any peaks of magnetic origin and were used to determine the crystal-structure parameters and instrumental scale factor. The atoms are in the

TABLE I. Comparison of calculated ( $I_c$ ) and observed ( $I_o$ ) relative nuclear intensities for  $\text{Ca}_2\text{MnO}_4$  at 200°K. Calculations made with  $z_{\text{Ca}} = 0.361$ ,  $z_{\text{O(I)}} = 0.164$ ;  $b_{\text{Mn}}$ ,  $b_{\text{Ca}}$ , and  $b_{\text{O}} = -0.36$ , 0.49, and  $0.577 \times 10^{-12} \text{ cm}$ , respectively.<sup>a</sup>

$hkl$	$I_c$	$I_o$
002	0.8	<2.0
101	25.5	23.5
004	18.4	17.0
103	45.1	53.1
110	18.2	24.7
112	407.5	400.3
114	587.5	620.7
200	243.6	241.6

<sup>a</sup> Neutron Diffraction Commission, Acta Cryst. **A25**, 391 (1969).

<sup>7</sup> B. O. Loopstra, Nucl. Instr. Methods **44**, 181 (1966).

following special positions of space group  $I4/mmm$ : Mn in  $2(a)$  at 000; Ca in  $4(e)$  at  $00z_1$ ; O(I) in  $4(e)$  at  $00z_2$ ; and O(II) in  $4(c)$  at  $\frac{1}{2}00$ . A least-squares refinement based upon eight observed peaks gave values for  $z_{\text{Ca}}$  of 0.361(3) and  $z_{\text{O(I)}}$  of 0.164(1). The figures in parentheses are standard deviations. The corresponding intensities are listed in Table I. Unlike the isostructural fluorides, preferred orientation does not appear to be significant in  $\text{Ca}_2\text{MnO}_4$ .

The 4.4°K data are shown in the top half of Fig. 1. The magnetic (100) and (101) peaks<sup>8</sup> characteristic of the  $\text{K}_2\text{NiF}_4$  magnetic structure did not appear; instead, a set of peaks of the type  $(10 \frac{l}{2})$  with  $l$  odd were observed. This demonstrates that antiferromagnetic coupling within the (00 $l$ ) sheets is retained, but that the stacking of the sheets in the  $c$  direction is different. Mn neighbors 12 Å apart along [001] have their moments antiparallel instead of parallel, with the consequence that the magnetic cell is double the chemical cell in this direction.

Intensity calculations confirm that this arrangement is indeed correct, and also that the moments are directed along the  $c$  axis as in  $\text{K}_2\text{NiF}_4$ . The structure is shown in Fig. 2, together with that of  $\text{K}_2\text{NiF}_4$  for purposes of comparison. Observed and calculated intensities are given in Table II, based upon a form factor for  $\text{Mn}^{4+}$  obtained by extrapolation of the Watson-Freeman theoretical calculations for Mn ions of lower valency,<sup>9</sup> and a moment of  $2.0 \mu_B$  per  $\text{Mn}^{4+}$  ion. The possible error in this value is estimated to be no more than  $0.3 \mu_B$ . The moment is therefore very significantly lower than the spin-only value of  $3 \mu_B$  expected for  $\text{Mn}^{4+}$ . This point will be discussed in more detail later.

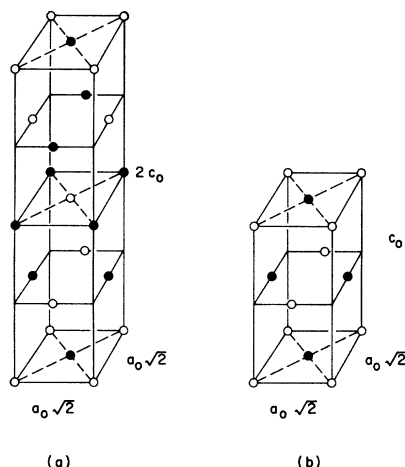


FIG. 2. Magnetic structure of (a)  $\text{Ca}_2\text{MnO}_4$ , (b)  $\text{K}_2\text{NiF}_4$ . Open and closed circles represent oppositely directed moments. Spin axis is along [001] in both cases. Only magnetic ions are shown.

<sup>8</sup> The indices of all magnetic peaks are based upon the  $\text{K}_2\text{NiF}_4$  magnetic unit cell, which has dimensions  $a_0\sqrt{2}$ ,  $c_0$  in terms of those of the chemical cell.

<sup>9</sup> R. E. Watson and A. J. Freeman, Acta Cryst. **14**, 27 (1961).

### III. TEMPERATURE-DEPENDENCE STUDIES

Diffraction data in the angular region  $25^\circ$ – $33^\circ$  were also collected at a number of temperatures in the range  $4.4$ – $200^\circ\text{K}$ . Unfortunately, the presence of a small impurity peak at about  $29.5^\circ$ , which is evident in the pattern in the top half of Fig. 1, introduced an additional uncertainty. This peak could perhaps be the (004) reflection from  $\text{Ca}_3\text{Mn}_2\text{O}_7$ , but in the absence of a detailed knowledge of the crystal structure, a positive identification could not be made. It did not appear to correspond to a magnetic peak from any simple magnetically ordered compound such as  $\text{CaMnO}_3$ ,  $\text{MnO}$ , or  $\text{Mn}_3\text{O}_4$ , for example, and it was also present in the  $200^\circ\text{K}$  and  $25^\circ\text{C}$  patterns, with the same intensity (as far as could be estimated). The intensity data shown in the lower half of Fig. 1 have therefore been plotted as difference patterns after subtraction of the  $200^\circ\text{K}$  data.

Although the intensities are quite weak, it is clear that there is a transition in the region of  $114^\circ\text{K}$ , in agreement with the sharp susceptibility maximum. Of particular interest is the behavior above this temperature. In spite of the poor statistics, the data are not altogether typical of normal critical scattering and there is a definite indication of peaking more at the (100) than the  $(10\frac{1}{2})$  position, with a relatively sharp "cutoff" below (100). This is qualitatively similar to the scattering from polycrystalline  $\text{K}_2\text{NiF}_4$ , and is consistent with the idea of very-long-range two-dimensional character which would be similar in both cases, since it is only in the stacking of the layers in the three-dimensional region that the two magnetic structures differ. However, the two-dimensional behavior is clearly not so well defined in  $\text{Ca}_2\text{MnO}_4$ .

TABLE II. Comparison of calculated ( $I_c$ ) and observed ( $I_0$ ) relative magnetic intensities for  $\text{Ca}_2\text{MnO}_4$  at  $4.4^\circ\text{K}$ . Indices are based upon a unit cell  $a_0\sqrt{2}$ ,  $c_0$  in terms of the chemical unit cell. Calculations based on the model in Fig. 2(a) with  $\mu_{\text{Mn}} = 1.99 \mu_B$  and the form factor described in text.

$hkl$	$I_c$	$I_0$
$10\frac{1}{2}$	38.0	37.9
$10\frac{3}{2}$	19.9	19.7
$10\frac{1}{2}$	7.8	8.1
$10\frac{7}{2}$	3.0	2.4

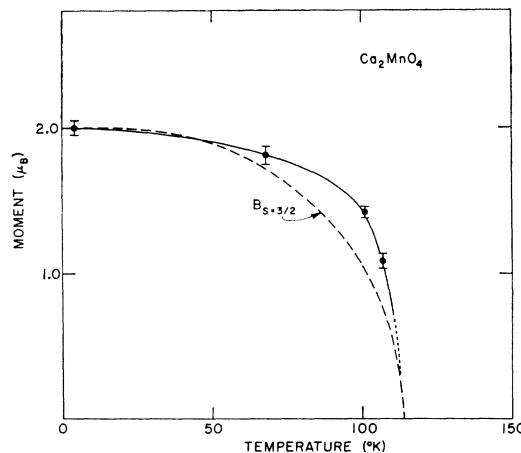


FIG. 3. Variation of ordered magnetic moment of  $\text{Ca}_2\text{MnO}_4$  with temperature. The broken line corresponds to the Brillouin function for  $S = \frac{3}{2}$ .

The variation of the ordered moment with temperature is shown in Fig. 3. It is not possible from this to make an accurate estimate of the Néel temperature, but the figure of  $114^\circ\text{K}$  obtained from susceptibility measurements represents a reasonable extrapolated value. The curve is noticeably steeper than the Brillouin function for  $S = \frac{3}{2}$  as it approaches  $T_N$ .

It is noteworthy that the value of the  $\text{Mn}^{4+}$  moment extrapolated to  $0^\circ\text{K}$  is only  $2.0 \mu_B$ . This may be compared to the value of  $2.65 \mu_B$  in  $\text{CaMnO}_3$ .<sup>10</sup> The difference between this latter value and the spin-only one of  $3 \mu_B$  could plausibly be attributed to covalency effects. The significantly larger difference in  $\text{Ca}_2\text{MnO}_4$  could possibly indicate a large zero-point spin deviation, which would amount to  $0.4 \mu_B$  in the limiting case of an ideal-ordered two-dimensional lattice.<sup>11</sup> However, Goodenough<sup>12</sup> has argued that while a localized electron model is appropriate for  $\text{CaMnO}_3$ , this may not be so in the case of  $\text{Ca}_2\text{MnO}_4$ , where conditions for collective electron antiferromagnetism are approached. Thus the significance of the low moment is open to question at present. It is hoped that similar investigations of other oxides of this type which are in progress will help clarify this point.

<sup>10</sup> E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

<sup>11</sup> P. W. Anderson, Phys. Rev. **86**, 694 (1952).

<sup>12</sup> J. B. Goodenough, Phys. Rev. **164**, 785 (1967).