

## Magnetism of Synthetic and Natural $\text{MnCO}_3$ †

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Weakly ferromagnetic  $\text{MnCO}_3$  powder with  $T_N=32.2^\circ\text{K}$  shows single-domain behavior with coercive force of about 3.5 kOe at  $4.2^\circ\text{K}$ . The differential susceptibility at dc and 10 MHz is less at low fields than at high fields for  $T<10^\circ\text{K}$ ; the remanent susceptibility is the same as the initial susceptibility. The measurements are consistent with a magnetization process involving spin flopping of the sublattices in the low-anisotropy basal plane. The measured remanent moment at  $4.2^\circ\text{K}$  indicates a spontaneous ferromagnetic moment of 92 emu/mole in pure  $\text{MnCO}_3$ . Natural crystals of composition  $\text{Mn}_{0.95}\text{Fe}_{0.05}\text{CO}_3$  (2.3% Fe by weight) show no weak ferromagnetism below  $T_N=35^\circ\text{K}$ . Instead, the spins are aligned parallel to the trigonal crystal axis, resulting in normal uniaxial antiferromagnetism. The large anisotropy of the  $\text{Fe}^{++}$  impurities is assumed to be the cause.

### I. INTRODUCTION

IN order to give better understanding of some, not yet published, rf susceptibility measurements on weakly ferromagnetic  $\text{KMnF}_3$ , part of the experiment was repeated with the weak ferromagnet  $\text{MnCO}_3$ , for which more complete susceptibility data<sup>1,2</sup> as well as theory<sup>3</sup> are available. When the rf measurements of both synthetic powder and natural crystals of  $\text{MnCO}_3$  showed large differences from the published data, direct measurements of the static magnetic moment of these materials were made for comparison. The rf results were confirmed.

The powder data show the expected weak ferromagnetism, but with much higher coercive forces involved in magnetization reversal than predicted from published work, which shows only a small anisotropy in the basal plane containing the magnetic sublattices and very small hysteresis of the remagnetization process in  $\text{MnCO}_3$  crystals.<sup>1</sup> An explanation based on a spin-flop magnetization process in single-domain particles is offered here.

It has also been observed that in a natural crystal containing 2.3-wt % Fe, the antiferromagnetic spin configuration is changed from one with the spins in the basal plane and a small canted spin component in that plane<sup>1,4</sup> as occurs in pure  $\text{MnCO}_3$ , to one where the spins are aligned parallel to the trigonal axis resulting in the disappearance of the weak ferromagnetism as predicted by theory.<sup>3</sup>

### II. EXPERIMENTAL DETAILS

The powder used in the experiments was Baker Analysed Reagent  $\text{MnCO}_3$  with a nominal 0.001-wt % Fe

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<sup>1</sup> A. S. Borovik-Romanov, *Zh. Eksperim. i Teor. Fiz.* **36**, 766 (1959) [English transl.: *Soviet Phys.—JETP* **9**, 539 (1959)].

<sup>2</sup> A. S. Borovik-Romanov and M. P. Orlova, *Zh. Eksperim. i Teor. Fiz.* **31**, 579 (1956) [English transl.: *Soviet Phys.—JETP* **4**, 531 (1957)].

<sup>3</sup> I. Dzyaloshinsky, *J. Phys. Chem. Solids* **4**, 241 (1958); *T. Moriya*, *Phys. Rev.* **120**, 91 (1960).

<sup>4</sup> R. A. Alikhanov, *Zh. Eksperim. i Teor. Fiz.* **36**, 1690 (1959) [English transl.: *Soviet Phys.—JETP* **9**, 1204 (1959)].

content, as specified by the manufacturer (J. T. Baker Chemical Co., Phillipsburg, N. J.); the color of the powder was a pale brown. The crystal was part of a rhodochrosite specimen from the McGill Redpath Museum. The synthetic powder and pulverized mineral were compared with an x-ray diffractometer and both structures were found to conform to that of rhodochrosite. Comparison of the diffraction linewidths for the two samples made possible an estimate of the chemical powder particle size; this was determined to be  $200 \text{ \AA} \pm 50\%$ .

An electron-microprobe analysis of the mineral showed that it contained  $(2.3 \pm 0.1)\%$  Fe by weight and less than the 0.1% detection limit of Ca, Mg, and Zn. These elements are the impurities to be expected in natural rhodochrosite.<sup>5</sup> Because of the naturally existing substitution series  $\text{MnCO}_3\text{—FeCO}_3$ , the Fe is assumed to be present as  $\text{Fe}^{++}$ , replacing  $\text{Mn}^{++}$  in the crystal lattice.

The rf differential susceptibility was measured at 10 MHz with a phase-locked magnetometer.<sup>6</sup> Continuous recordings were made of the inductance changes in a coil containing the sample while the sample temperature was varied by means of cold-helium gas flow. The temperature was measured with a calibrated copper-constantan thermocouple attached to the sample; the accuracy is estimated to be within  $0.2^\circ$  above  $20^\circ\text{K}$ . The magnetic background owing to the thin thermocouple wire was subtracted from the measurements.

The static magnetic moment of the  $\text{MnCO}_3$  was found in fields up to 13.5 kOe by means of a commercial vibrating-sample magnetometer. This part of the experiment was carried out with the cooperation of Dr. J. A. MacKinnon at Sir George Williams University. Temperatures were measured with a thermocouple in the He gas flow near, but not on the sample; as a result, accuracy greater than  $\pm 2^\circ\text{K}$  is not expected. Moments were measured at fixed temperatures as the external field was varied.

<sup>5</sup> W. A. Deer, R. A. Howie, and J. Zussmann, *Rock-Forming Minerals* (Longmans Green & Co., Ltd., London, 1962), Vol. 5, p. 265.

<sup>6</sup> I. Maartense (unpublished).

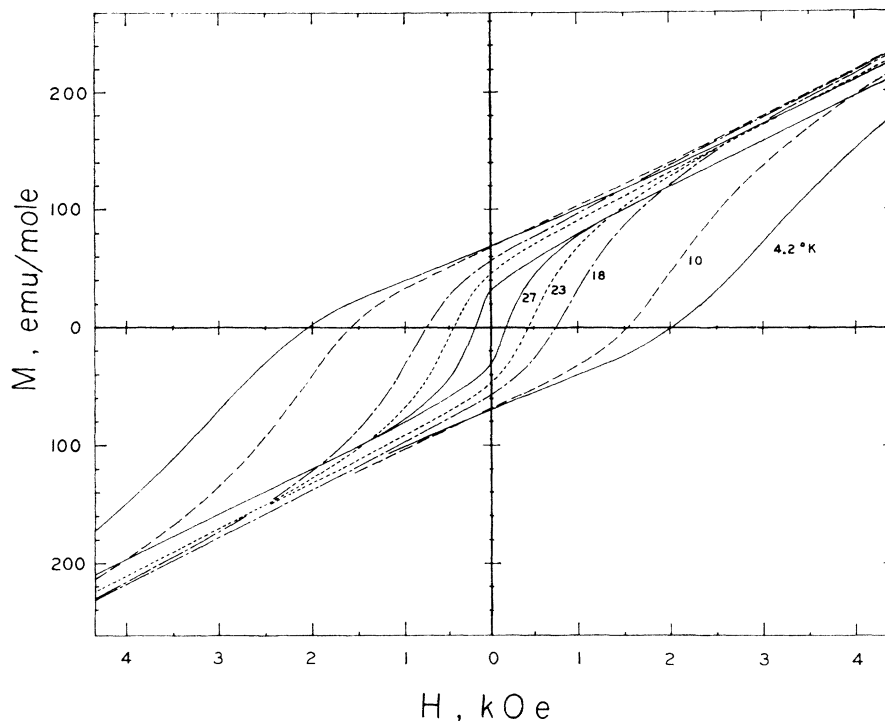


FIG. 1. Hysteresis loops of  $\text{MnCO}_3$  powder at the temperatures indicated. Maximum applied field  $H$  in all cases was 13.5 kOe. For clarity, experimental points and parts of the descending branches on the left have been omitted.

In both experiments, the powder sample was in the form of a pellet of synthetic beeswax containing about 20%  $\text{MnCO}_3$  by volume. For the rf measurements, crystal samples were aligned visually, using their rhombohedral faces. The smaller sample used in the moment measurements was oriented by x-ray diffraction. In this case the crystal was mounted so that the external field could be rotated in a plane containing the trigonal  $c$  axis.

### III. RESULTS

Hysteresis loops of  $\text{MnCO}_3$  powder for several temperatures are shown in Fig. 1. The maximum applied field  $H$  was 13.5 kOe for all curves. The high values of the coercive force  $H_c$  and its temperature dependence are clearly visible. Here,  $H_c$  may be defined as the field at which the magnetization  $M = \chi_a H$  intersects the hysteresis loop, where  $\chi_a$  is the antiferromagnetic component of the low-field susceptibility. The magnetization curves (not shown in Fig. 1) starting at  $M, H = 0$  fall halfway between the upper and lower parts of the hysteresis loops at any value of  $H$ . A complete magnetization curve and hysteresis loop are shown by the broken curves in Fig. 5.

It is also apparent from Fig. 1 that at low temperatures the slope of the curves is less at low fields than it is at high fields, with the result that the saturation moment  $M_s$  deduced by extrapolation of the high-field magnetization is less than the measured remanent moment  $M_R$  by a factor of about  $\frac{3}{4}$  at 4.2°K, and, in fact, is less than the extrapolated moment at temperatures as high

as 20°K. Then, taking  $M_R = 0.60$  emu/g = 69 emu/mole at 4.2°K as the spontaneous ferromagnetic moment of the  $\text{MnCO}_3$  powder, is practically the same as 68 emu/mole, estimated by Borovik-Romanov and Orlova.<sup>2</sup> These authors found it necessary to make a 15% weight correction because of adsorbed water in their sample of commercial  $\text{MnCO}_3$  powder; it is believed that any such correction is not necessary in the present case. Although the largest field used in Ref. 2 was about 2.5 kOe, this should have been sufficient for saturation of the sample at the lowest reported temperature of 15°K, especially if the sample was cooled through the Néel point in a field of several hundred Oe (see below).

The main features of the hysteresis loops can be seen clearly when differential susceptibility  $\chi = dM/dH$  is plotted against  $H$ , as in Fig. 2, which was obtained by taking differences between the measured values of  $M$  and  $H$ . These curves are drawn so that the magnetic field changes towards the right. The peaks in the susceptibility,  $\chi_{\max}$ , occur at field values about 15% less than  $H_c$  as defined above. At high fields,  $\chi$  increases somewhat as the temperature is lowered, in agreement with Ref. 1. The initial susceptibility  $\chi_0$  decreases with decreasing temperature  $T$ , because of the shift of the peaks of  $\chi(H)$ . For  $T < 10^\circ\text{K}$ ,  $\chi_0$  is less than  $\chi$  at high fields; the reason for this will be discussed below.

The differential susceptibilities obtained from the magnetization curves show the same  $\chi_0$  as is found from the hysteresis loops, and for  $H > 0$ ,  $\chi$  is the average of the values of  $\chi$  shown in Fig. 2 for the same fields on the left and right of  $H = 0$ . The field at  $\chi_{\max}$  is the same as in the case of full magnetization reversal.

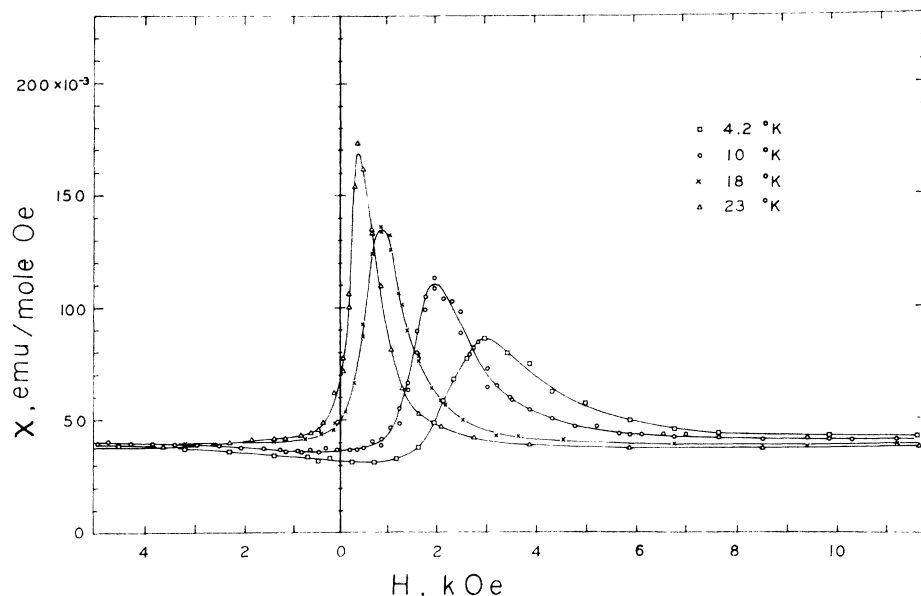


FIG. 2. Measured differential susceptibility of  $\text{MnCO}_3$  powder for several temperatures below  $T_N$ . The values of  $\chi = dM/dH$  were derived from the data used in Fig. 1. The applied field  $H$  is changing towards the right.

Because of the uncertainty in the temperature measurements, it was not feasible to determine accurately the temperature variations of the magnetic anisotropy involved in the reversal of magnetization, as represented by  $H_c$  or  $H$  at  $\chi_{\text{max}}$ . Near the Néel point  $T_N$ , the anisotropy is low as expected; an indirect measure of this can be obtained from the data in Fig. 3. These represent the remanent moment produced when the  $\text{MnCO}_3$  powder is cooled through  $T_N$  to  $4.2^\circ\text{K}$  in the external field shown. This moment appears to approach a value near  $\frac{3}{4}M_R$  at  $4.2^\circ\text{K}$ , although the biasing field was not taken high enough to be certain of this. However, it is clear that a field of 10 Oe applied above  $T_N$  is sufficient to cause orientation of at least half of the weak ferromagnetic moments of the powder particles in the direction of the applied field, when cooled below  $T_N$ . This field is about the same as the internal field

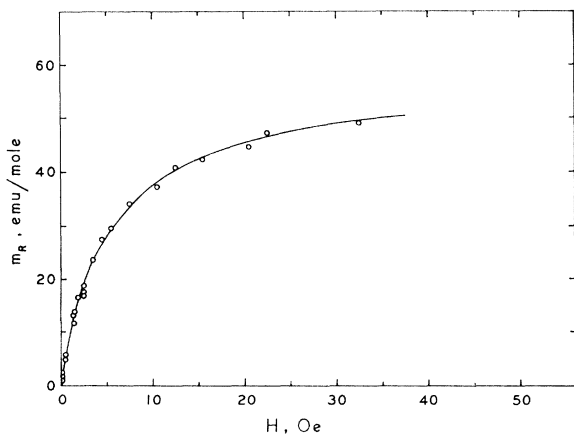


FIG. 3. Remanent moment  $m_R$  in  $\text{MnCO}_3$  powder at  $4.2^\circ\text{K}$ , produced by cooling through  $T_N$  in a small applied field  $H$ .

$4\pi M_s$  of a single-domain particle with a net moment  $M_s$  per unit volume; at  $T_N - 2^\circ\text{K}$ ,  $M_s$  is already near 40% of the value at  $T=0$ , as seen from the ordering curve.<sup>1</sup> It shows that a low-anisotropy energy barrier, represented by  $\frac{1}{2}MH < 10^{-21}$  erg/ion, exists below  $T_N$ .

It should be obvious that, because a state of saturation of the weak moment at a given temperature can be achieved in at least two ways, curves of  $\chi(H)$  at constant temperature such as Fig. 2 can not be used to predict  $\chi(T)$  at constant field, except in the special case  $H=0$ .

The initial susceptibilities seen in Fig. 2 are compared in Fig. 4(a) with the rf susceptibilities measured at 10 MHz in ambient field ( $\lesssim 1$  Oe). The rf data were obtained relative to an arbitrary baseline, and in Fig. 4(a) they are scaled to fit the static susceptibilities derived from moment measurements above  $T_N$ . The qualitative agreement below  $T_N$  is seen to be good. The rf curve falls below the static points as  $T_N$  is approached; this is to be expected because the magnetic moment changes become less reversible in the rf field as the hysteresis loop becomes narrower near  $T_N$  (i.e., when the experimental conditions correspond to operation closer to  $\chi_{\text{max}}$  of Fig. 2).

The powder susceptibility around  $T_N$  is shown on an expanded temperature scale in Fig. 4(b). If the extrapolation of the curve as shown is used to define the Néel point, the value of  $T_N = 32.2^\circ\text{K}$  so obtained is within experimental error of  $T_N = 32.4^\circ\text{K}$  measured by Borovik-Romanov.<sup>1</sup> The peak in the rf susceptibility occurs at  $30.7^\circ\text{K}$ ; it can be assumed that in the temperature region below this, the variation in  $\chi$  is determined mainly by a changing magnetic anisotropy  $K$ , as in Fig. 2, whereas above this temperature the effect of the changing weak moment  $M_s$  established by magnetic

ordering is predominant. The peak in  $\chi$  then corresponds to a minimum in  $K/M_s^2$  as a function of temperature.<sup>7</sup>

A paramagnetic Curie temperature  $\theta = -68^\circ\text{K}$  is indicated from a plot of  $\chi^{-1}$  for the  $\text{MnCO}_3$  powder above  $60^\circ\text{K}$ , which is close to  $\theta = -64.5^\circ\text{K}$  found by Borovik-Romanov and Orlova.<sup>2</sup>

The straight lines through the origin in Fig. 5, representing the magnetic moments parallel and perpendicular to the  $c$  axis of the natural rhodochrosite crystal, show the absence of a spontaneous moment in this material when it contains 2.3% iron. The nearly constant value of  $\chi_{\perp}$  below  $T_N$  and the vanishing of  $\chi_{\parallel}$  as  $T \rightarrow 0$  confirm the classic uniaxial antiferromagnetic behavior observed in the rf measurements of Fig. 4(a). The rf data were again normalized to the static susceptibility above  $T_N$ . The anisotropy with  $\chi_{\parallel} > \chi_{\perp}$  above  $T_N$  was not observed in purer  $\text{MnCO}_3$  crystals,<sup>1</sup> and here it must be due to the presence of iron. Indeed, the anisotropy of 1.9% at  $300^\circ\text{K}$  compares closely with that predicted by Krishnan and Banerjee<sup>8</sup> for  $\text{MnCO}_3$  with iron impurities.

From the rf curves, the Néel point of the impure  $\text{MnCO}_3$  crystal is found to be  $35^\circ\text{K}$ . The data above  $T_N$  show that  $\theta = -70^\circ\text{K}$  for  $\chi_{\parallel}$  and  $\theta = -64^\circ\text{K}$  for  $\chi_{\perp}$ . These values and  $\theta = -68^\circ\text{K}$  for pure powder are within experimental error of each other and that given in Ref. 2.

Figure 6 shows the magnetic moment of the  $\text{MnCO}_3$  crystal at  $4.2^\circ\text{K}$  as an external field of 2.7 kOe is rotated in a plane containing the trigonal axis. The drawn curve is the function  $M_{\perp} \cos^2\theta$ , where  $M_{\perp}$  is the moment when the applied field is in the basal plane, and  $\theta$  is the angle between the field and the  $c$  axis. These measurements again establish that the crystal behaves as an ordinary antiferromagnet with the direction of easy magnetization of the two sublattices parallel to the trigonal axis.

#### IV. DISCUSSION

It appears certain that the small size ( $\sim 200 \text{ \AA}$ ) of the  $\text{MnCO}_3$  powder particles ensures their single-domain behavior, although this is difficult to prove explicitly. Assuming a low value of  $\sigma_w = 10^{-3} \text{ erg/cm}^2$  for the domain-wall energy density<sup>9</sup> and comparing this to the magnetostatic energy of a particle, a critical radius for wall formation is given by<sup>10</sup>

$$R_c = (9/4\pi)(\sigma_w/M_s^2) \approx 10^{-4} \text{ cm}.$$

Since this is probably a low estimate, there can be little doubt that the present powder results reflect the proper-

<sup>7</sup> J. Smit and H. P. J. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959).

<sup>8</sup> K. S. Krishnan and S. Banerjee, *Z. Krist.* **99**, 499 (1938).

<sup>9</sup> J. A. Eaton, A. H. Morrish, and C. W. Searle, *Phys. Letters* **26A**, 520 (1968).

<sup>10</sup> C. Kittel and J. K. Galt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 506.

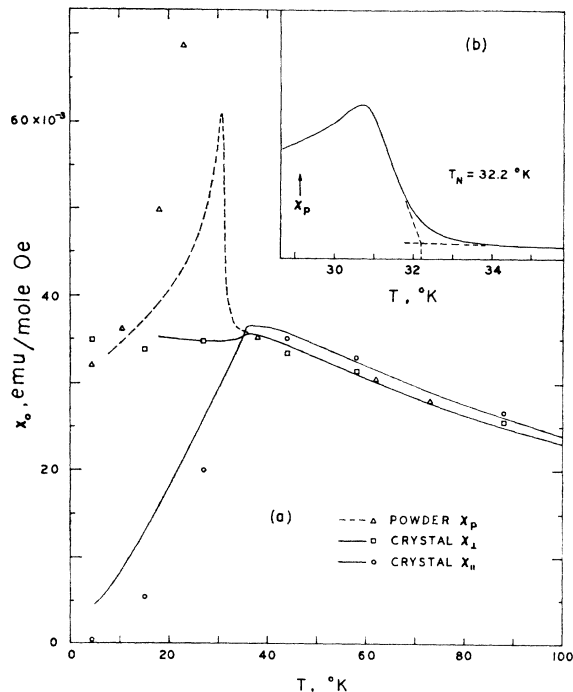


Fig. 4. (a) Comparison of  $\chi_0$  at 10 MHz (curves) and the static  $\chi_0$  (points) as a function of temperature for  $\text{MnCO}_3$  powder (broken curve) and  $\text{Mn}_{0.95}\text{Fe}_{0.05}\text{CO}_3$  crystal (solid curves);  $\chi_{\perp}$  and  $\chi_{\parallel}$  are referred to the trigonal axis;  $\chi_{\parallel}$  shows an error in crystal alignment. (b) Powder  $\chi_0$  at 10 MHz on expanded scale, showing  $T_N$ .

ties of single-domain particles of  $\text{MnCO}_3$ . This assumption is important because, in the explanation of the results which follows, the magnetization of the powder sample does not involve domain-wall motion.

The observed coercive forces are large compared to the internal field  $4\pi M \approx 30 \text{ Oe}$ , so that no corrections to the applied field are necessary. For the same reason, the effects of shape anisotropy of the particles can be neglected.

Perhaps the most relevant information contained in the powder hysteresis curves is the low value of the initial susceptibility at low temperatures, relative to the high-field susceptibility (Fig. 2). While this effect may be related to the anomalous low-field behavior of  $M_{\parallel}$  discussed by Borovik-Romanov,<sup>1</sup> it is felt that a more likely cause lies in a mechanism analogous to that suggested by Lee *et al.*<sup>11</sup> for  $\text{CsMnF}_3$  (which has the  $\text{Mn}^{++}$  spins in the basal plane with low anisotropy but with no net canting).

If, at low fields, the sublattice magnetizations are tied to their preferred directions in the basal plane by the small but finite anisotropy in that plane, the powder susceptibility will be similar to that of a uniaxial antiferromagnet, with a low, but nonzero,<sup>12</sup> value of  $\chi_{\parallel}$  at  $T=0$ . The aligning of the canted moments would

<sup>11</sup> K. Lee, A. M. Portis, and G. L. Witt, *Phys. Rev.* **132**, 144 (1963).

<sup>12</sup> R. Orbach, *Phys. Rev.* **115**, 1189 (1959).

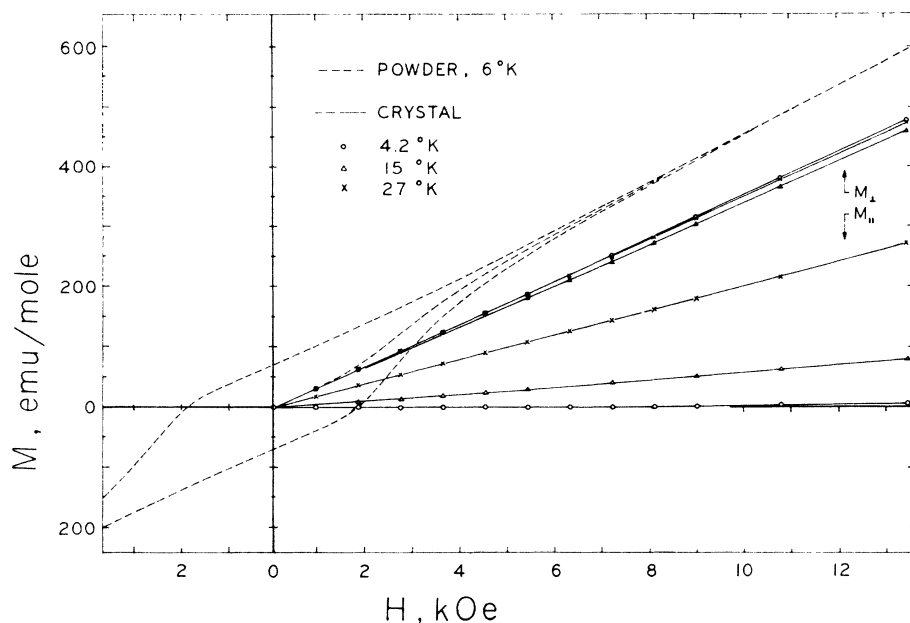


FIG. 5. Solid lines are the  $M$ - $H$  curves of natural crystal at various temperatures below  $T_N$ ;  $M_{11}$  and  $M_1$  are referred to the trigonal axis. Broken curves show a complete magnetization curve and hysteresis loop of  $\text{MnCO}_3$  powder.

occur by means of flopping of the sublattice spins in the basal plane, rather than by simple rotation of the weak ferromagnetic component in the applied field. The critical field  $H_F$  for spin flopping, in terms of the molecular exchange field  $H_E$  and the anisotropy field  $H_A'$  in the basal plane, is given as usual by  $H_F = (2H_E H_A')^{1/2}$ . From resonance experiments,  $H_F$  is found to be 1.4 kOe at 4.2°K by Date<sup>13</sup> and somewhat less by Shaltiel.<sup>14</sup>  $H_F$ , as defined here, is the minimum external field required in the basal plane, as  $T \rightarrow 0$ , when  $H_F$  is parallel to an easy axis. For randomly oriented particles, the average spin-flopping field is, course, higher; this average field then corresponds to the applied field at  $\chi_{\max}$  in Fig. 2.

When the field is reduced, spin flops in individual particles are expected to return the sublattices without hysteresis to the nearest easy direction in the basal plane. The weak moment, however, will have a com-

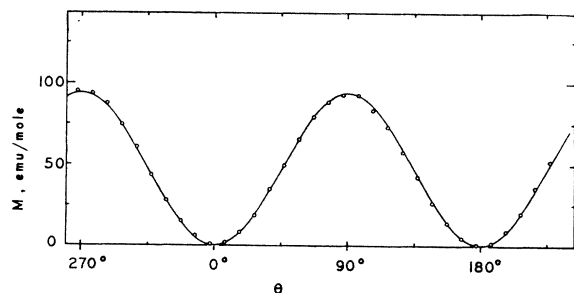


FIG. 6. Moment of crystal at 4.2°K as a field of 2.7 kOe is rotated through  $c$  axis ( $\theta=0^\circ$ ) and basal plane ( $\theta=90^\circ$ ). The solid curve is  $M = M_1 \cos^2 \theta$ .

<sup>13</sup> M. Date, J. Phys. Soc. Japan 15, 2251 (1960).

<sup>14</sup> D. Shaltiel, Phys. Rev. 142, 300 (1966).

ponent remaining parallel to the applied field. At zero field the average remanent moment of the powder will be  $\frac{3}{4}$  of the saturation value of the weak ferromagnetic moment.<sup>7</sup> The remanent susceptibility will be the same as the initial susceptibility, and the magnetization curve will lie midway between the ascending and descending branches of the major hysteresis loop, in agreement with the observations. As expected, the differential susceptibility begins to return to its remanent value in the field region corresponding to the average spin-flopping fields (left side of Fig. 2). The temperature variation of the coercive force seen in Figs. 1 and 2 should be due to the variation of the flopping field, so that approximately  $H_c^2 \propto H_A'$ . At the higher temperatures, thermal agitation will cause some spin flopping even in zero field, accounting for the rise in  $\chi_0$ .

While the present measurements are consistent with the magnetization process just described, the measurements of Borovik-Romanov<sup>1</sup> seem to be contradictory. However, the lack of appreciable hysteresis observed in the magnetization of a  $\text{MnCO}_3$  crystal can be ascribed to domain effects. The low-field part of the magnetization curve is not shown in detail in Ref. 1, but it is evident that saturation takes place at a field consistent with the spin-flopping mechanism rather than one of simple spin rotation.

The spontaneous moment near  $T=0$  of 188 emu/mole, reported by Borovik-Romanov for a natural  $\text{MnCO}_3$  crystal, is to be compared to the powder value of  $\frac{4}{3} \times 69 = 92$  emu/mole at 4.2°K. Whether the difference by a factor of 2 in these results is due to size or shape effects in the powder or impurities in the crystal or to other factors can not be determined at present.

Turning now to the results for Fe-containing  $\text{MnCO}_3$ , it can be said that, because of the near equality of the paramagnetic Curie temperature ( $\theta \approx 66^\circ\text{K}$ ) in the powder and the crystal, it is shown that the superexchange interaction in  $\text{MnCO}_3$  is affected only slightly by the addition of Fe impurities. The Néel point is raised from 32.2 to 35°K by 2.3% by weight of Fe (pure  $\text{FeCO}_3$  has  $T_N \approx 38^\circ\text{K}$ <sup>15</sup>), so that the effective exchange field is a little greater than in pure  $\text{MnCO}_3$ . This probably accounts partly for the lower value of  $\chi_1$  of the crystal below  $T_N$ , compared to the high field  $\chi$  of the powder (Figs. 4 and 5).

While the impurities have little effect on the interaction giving rise to magnetic ordering, they can have a profound influence on the resulting spin configuration through their effect on the magnetic anisotropy. The anisotropy fields, in general, do not have the same origin as the exchange fields; in  $\text{MnCO}_3$ , the main source of the anisotropy energy can be found in the long-range magnetic-dipolar interaction.<sup>16</sup> A calculation of this interaction in hexagonal  $\text{CsMnF}_3$  by Lee *et al.*<sup>11</sup> has shown that it can account for most of the observed anisotropy and causes the spins to align parallel to the basal plane. Sufficient anisotropy energy of the opposite sign must be contributed by the Fe impurities to align the spins parallel to the  $c$  axis. A rough estimate of this additional anisotropy is  $5 \times 10^{-16}$  erg/ion average for all  $\text{Mn}^{++}$  ions, or  $10^{-14}$  erg/ion of  $\text{Fe}^{++}$  in the present substitution ratio of 1:20; this is of the same order as the exchange energy.

It is known that in  $\text{FeCO}_3$  the spin configuration is parallel to the  $c$  axis,<sup>4</sup> and that the spins are tightly bound to this axis by a large anisotropy field. This is shown by the large anisotropy in the susceptibility above  $T_N$  and by the metamagnetic transition in a field of 200 kOe.<sup>15</sup> The cause of this is a highly anisotropic  $g$  factor resulting from the action of the trigonal crystalline field on the orbital doublet ground state of the  $\text{Fe}^{++}$  ions.<sup>17</sup> The anisotropy energy should thus be of a magnitude similar to the isotropic exchange energy.<sup>18</sup> It is then easy to see how an Fe:Mn ratio of 1:20 is sufficient to cause a net positive uniaxial anisotropy by overcoming the small negative dipolar anisotropy. The minimum Fe content required to change the spin configuration of  $\text{MnCO}_3$  from the basal plane to the  $c$  axis is not apparent from the available data. The measurements show that for 2.3-wt %  $\text{Fe}^{++}$  content the spin-flop field parallel to the  $c$  axis is greater than 14 kOe, so that the average uniaxial anisotropy is at least 300 Oe.

It may be noted that in the case of six nearest-neighbor exchange, a substitution ratio of 1:124, corresponding to 0.4% Fe content by weight, will ensure

that on the average each Mn ion will have an Fe nearest or next-nearest neighbor. Below the concentration at which the spins begin to flip parallel to the  $c$  axis, there will be localized distortions of the  $\text{Mn}^{++}$  spin configuration out of the basal plane, leading to a gradual change in the weak ferromagnetic moment. Slightly above the critical concentration, the net anisotropy will be low so that spin flopping back into the basal plane should occur for low fields applied along the  $c$  axis. In all cases, the  $\text{Fe}^{++}$  spins will remain parallel to the  $c$  axis.

The contributions to the anisotropy from the dipole-dipole interactions of the  $\text{Mn}^{++}$  and from the crystal-field interactions with the  $\text{Fe}^{++}$  ions may be expected to vary at different rates with temperature so that it is quite likely that for some Fe-doping concentration an antiferromagnetic to weak ferromagnetic transition will take place somewhere below  $T_N$ , even in zero applied field.

## V. CONCLUSIONS

The magnetic measurements of  $\text{MnCO}_3$  powder agree with those of Borovik-Romanov and Orlova.<sup>2</sup> The apparent discrepancy in the susceptibility data is evidently due to their use of  $M/H$  values, instead of the differential susceptibility  $dM/dH$  reported here.

In addition, the present results are consistent with an assumption that in single-domain particles, the magnetization process in the weak ferromagnet  $\text{MnCO}_3$  is predominantly one of spin flopping of the sublattice magnetizations in the basal plane. In particular, this mechanism explains the low value of  $\chi_0$  at low temperatures and the equality of  $\chi_0$  and  $\chi_{\text{rem}}$ . Thus, at low temperatures,  $\chi_0$  becomes the antiferromagnetic powder susceptibility, which is independent of the magnetic history of the sample.

A crystal of composition  $\text{Mn}_{0.953}\text{Fe}_{0.047}\text{CO}_3$  shows classic uniaxial antiferromagnetism with the spins aligned parallel to the  $c$  axis instead of lying in the basal plane with a net canted moment.<sup>1</sup> The large effect of  $\text{Fe}^{++}$  ions on the spin configuration is considered to be due to their large, positive anisotropy energy which swamps the relatively small magnetic anisotropy of the host  $\text{Mn}^{++}$  ions. The Fe content (0.001%) of the  $\text{MnCO}_3$  powder sample was too low to cause any observable magnetic effects of this nature.

This preliminary investigation points to the desirability of carrying out further studies of the properties of Fe-substituted  $\text{MnCO}_3$ . Synthetic powder with various Fe dopings should be easy to prepare. If crystals of these compounds can be grown,<sup>19</sup> interesting spin-flop studies should be possible, including magneto-optical and spectroscopic experiments. The change of direction of the sublattice magnetizations from the basal plane to the trigonal axis may also have important effects on the spin-wave spectrum.<sup>1</sup>

<sup>15</sup> I. S. Jacobs, *J. Appl. Phys.* **34**, 1106 (1963).

<sup>16</sup> H. J. Fink and D. Shaltiel, *Phys. Rev.* **130**, 627 (1963).

<sup>17</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **20**, 890 (1958).

<sup>18</sup> T. Nagamiya, K. Yosida, and R. Kubo, *Advan. Phys.* **4**, 1 (1955).

<sup>19</sup> N. Y. Ikornikova, *Kristallografiya* **6** (1961) [English transl.: *Soviet Phys.—Cryst.* **6**, 594 (1962)].

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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).