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Study of some magnetic properties of a mixed phase (Mn_3O_4) in MnO crystals

M. S. Jagadeesh and Mohindar S. Seehra
Department of Physics, West Virginia University, Morgantown, West Virginia 26506
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Magnetic susceptibility and magnetization measurements have been carried out on several samples of MnO in the temperature range of 4.2 to 300 K and in magnetic fields up to 10 kOe using the Faraday technique. The measurements were done on four commercial single crystals, a powder MnO specimen (pure MnO), and an annealed MnO single crystal. All four commercial crystals were found to contain significant amounts (2 to 8%) of Mn_3O_4, a ferrimagnet with $T_c \simeq 43$ K. Hence, the Mn_3O_4 impurity in these samples completely dominates the magnetic properties at lower temperatures. The impurity concentrations are estimated from observed magnitudes of the spontaneous moment, and confirmatory evidence is obtained from x-ray analysis of the samples. A displaced hysteresis loop has been observed at 4.2 K, suggesting the presence of exchange anisotropy at the ferrimagnetic-antiferromagnetic (Mn_3O_4–MnO) interfaces. Annealing of a commercial crystal in Mn atmosphere (using an evacuated sealed quartz tube) at 1293 K for about 200 h is shown to convert the Mn_3O_4 impurity to MnO, thus yielding a pure single crystal of MnO.

I. INTRODUCTION

The first-row transition-metal mono-oxides remain of fundamental interest since their electronic properties have defied simple explanations.[1] Various properties of manganese mono-oxide, MnO, have been under investigation for over fifty years now. From magnetic-susceptibility, specific-heat, and strain data it became known quite early[2–4] that MnO undergoes a transition to an antiferromagnetic state below the Néel temperature $T_N \simeq 120$ K. From neutron diffraction measurements, the magnetic structure of MnO has been found to consist of ferromagnetic (111)-type sheets, with the neighboring (111) planes stacked antiferromagnetically along a [111] direction.[5] The antiferromagnetic ordering is accompanied by a rhombohedral distortion of the high-temperature fcc structure.[6] Recently it has been proposed that the transition to the antiferromagnetic states in MnO and NiO should be of first order.[7,8] Although a number of recent investigations[9–11] have shown the transition in MnO to be of first order, the same has not been found to be true in NiO, where the transition clearly appears to be of second order.[12]

Magnetic-susceptibility (χ) measurements on powdered MnO specimens (usually obtained by the decomposition of $MnCO_3$) have been performed by several groups, near or below T_N[3,11,13] and above room temperature.[14] The only reported χ measurements on a single crystal have been those of McGuire *et al.*[15] In these studies, χ was found to depend on applied magnetic field H below T_N and in the case of single-crystal studies,[15] even above T_N. Perhaps the most careful analysis of the data on a powder specimen has been that of Bloch *et al.*[13] in the temperature range of 4.2 to 200 K and in H up to 50 kOe. In their study χ was found to be independent of H above T_N and to increase with increasing H below T_N. From the latter, these authors estimated $\chi_\perp(4.2\text{ K}) = 79 \times 10^{-6}$ cm^3/g, whereas $\chi_{\max}(T \sim T_N) = 83 \times 10^{-6}$ cm^3/g.

In the single-crystal studies by McGuire *et al.*,[15] χ at 4.2 K was found to be irreproducible, and it was suggested that this might be due to the presence of a magnetic impurity, perhaps Mn_3O_4. However, no further work to prove the presence of the Mn_3O_4 phase in single crystals of MnO (usually grown by the flame fusion method) has since been carried out, although these crystals in recent years have been used in a number of other investigations.[9,10,16,17] Furthermore, no direct measurements of the principal susceptibilities of MnO have yet been carried out. The present work was undertaken to fill this gap. Our initial measurements on a single crystal of MnO at 4.2 K clearly indicated the presence of a ferromagnetic-type impurity, not too different from the observations of McGuire *et al.*[15] Following this, we obtained single crystals of MnO from four different sources and found similar observations in all of them. Since these crystals have been used around the world for many other investigations for the properties of pure MnO, it was thought to be extremely important to establish the nature and magnitude of this magnetic impurity in MnO single crystals and determine its effect on the magnetic properties of pure MnO. In this work, we provide evidence that the impurity is indeed Mn_3O_4 and its concentrations are on the order of few atomic percent. However, since Mn_3O_4 is ferrimagnetic with $T_c \simeq 43$ K,[18,19] even such a small concentration completely dominates the magnetic properties at the lower temperatures and even has noticeable effects near and above T_N. The exchange anisotropy, usually present due to ferromagnetic-antiferromagnetic interfaces,[20] has also been observed. The magnetic susceptibility of a relatively pure MnO powder has also been studied for comparison purposes. Finally, a successful experiment in which, an impure MnO single crystal with Mn_3O_4 impurity, has been converted to a pure MnO crystal, is described. The results of these studies are presented and discussed in this paper.

II. EXPERIMENTAL DETAILS

The measurements of magnetizations and magnetic susceptibilities presented in this paper were carried out by the Faraday technique, using a Cahn RG electrobalance, Lewis field-gradient coils, and a Janis cryostat. The details of the experimental apparatus and procedures are described elsewhere.[21] The samples used in these studies are listed in Table I, along with their sources. The samples, initially in the form of single crystals (except sample E, which was obtained in the powder form) were powdered with a mortar and pestle to about 100-μm size, were mounted in a platinum boat and covered with Duco cement before being suspended in the cryostat for the measurements. The corrections for the platinum boat and the Duco cement are less than 1% and have been disussed in detail elsewhere.[21] We chose to carry out ur initial measurements on powder samples in order o avoid complications due to anisotropies and econdly, the most important point, to facilitate comparison with the results of a relatively pure MnO powder (sample E). Most of the temperature-dependent measurements were carried out at 1 kOe, although fields up to 10 kOe were available. The data on each sample was usually taken in the temperature range of 4.2 to 300 K.

III. RESULTS AND ANALYSES

The variation of χ with temperature T, for samples A through E of Table I, is shown in Fig. 1. There are noticeable differences in the absolute magnitudes of χ for some of the samples above T_N(~120 K). Below about 70 K, χ for samples A through D increases whereas for sample E, χ continues to decrease. Our data on sample E are quite similar to the observation of Bloch *et al.*,[13] who had carried out measurements on the *same* sample. The small increase in χ observed below about 30 K may be due to the presence of a minute quantity of a paramagnetic impurity. Such a rise is not evident from the observation of Ref. 13 at low fields; however, they had only two data points below 50 K. A somewhat similar rise, observed in CoO samples by Seehra and Silinsky,[22] has been attributed to nonstoichiometry (cation deficiencies). It is quite unlikely that this rise is due to the presence of Mn_3O_4 since that leads to the presence of remanent magnetization. This was not observed in sample E, although an increase of χ with increasing H is observed, similar to the observation of Bloch *et al.*[13] This has been discussed in detail in Ref. 13 and this field dependence was atttributed to domain-wall rotation. Above T_N, χ was observed to

TABLE I. Summary of some results for various samples of MnO.

Sample	Source	T_N (K)	χ at 130 K (10^{-6} cm^3/g)	M_s at 4.2 K (cm^3 Oe/g)	at.% of Mn_3O_4 estimated	Identification of Mn_3O_4 by x-ray diffraction
A	Atomergic Chemical Co. U. S. A.	119.6	83.90	1.485	7.9	yes
B	Alfa-Ventron Corporation U. S. A.	117.0	80.00	0.950	5.1	yes
C	Nakazumi Crystals Japan	117.6	80.75	0.625	3.3	yes
D	Cristal-Tec Grenoble, France	118.6	82.00	0.380	2.0	yes
E	General Electric U. S. A.	119.0	79.85	nil	nil	no
F	Annealed Sample D	118.0	82.36	nil	nil	no

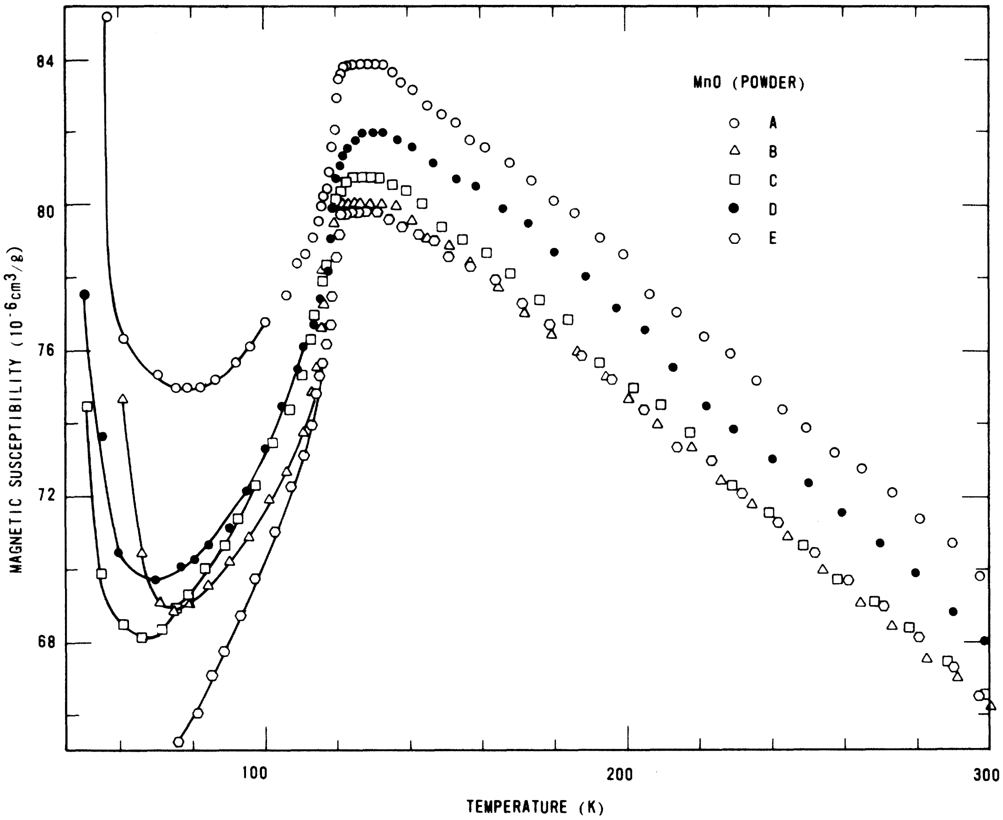

FIG. 1. The temperature variation of magnetic susceptibility for MnO powder samples obtained from five different sources (Table I). The increasing susceptibility below 80 K is shown by the lines drawn through the data points for clarity.

be independent of H (up to 10 kOe), within an accuracy of better than 0.4%, for all the samples.

Next we consider the determination of the T_N's for various samples from the data shown in Fig. 1. It is known that in antiferromagnets, the singularity in $d(\chi T)/dT$ is similar to that in the specific heat, and in MnF_2 this yielded T_N quite accurately.[23] Therefore, we used a similar procedure in MnO. $d(\chi T)/dT$ was obtained by computer fitting the data in the temperature range of 105 and 125 K to a second-order polynomial, choosing a four-point interval at a time, and evaluating $d(\chi T)/dT$ at median temperature. As an example, the results for sample E are shown in Fig. 2, and T_N's so determined are listed in Table I. The Néel temperatures so determined[24] are about 0.5 K lower than the temperatures at which a near discontinuity in χ occurs. We will return to the discussion of T_N's and their variations with samples later.

For samples A through D, obtained by powdering the four commercial single crystals, remanent magnetization was observed below about 50 K, which increased in magnitude as the temperature was lowered. To get at the spontaneous magnetization M_s at different temperatures for the various samples, the M vs H plots were extrapolated to $H=0$. The results so obtained are plotted in Fig. 3 for samples A to D and the M_s values at 4.2 K are listed in Table I. Since it is known that Mn_3O_4 is a ferrimagnet with $T_c=43$ K,[18,19] the results of Fig. 3 are consistent with Mn_3O_4 being an impurity in the MnO crystals A through D. Using a saturation moment[19] of 18.8 cm^3Oe/g for Mn_3O_4, the estimated concentrations of Mn_3O_4 in various samples of MnO are listed in Table I. If we use the value of 35.0 cm^3Oe/g for the saturation moment as determined by Jacobs[18] from the high-field studies, the estimated concentrations would be reduced by a factor of nearly 2. In any case, the important point is that Mn_3O_4 has been found to be present at the level of several percent in all commercially obtained single crystals.

In most cases, the samples were cooled from 77 to 4.2 K in a field of 1 kOe. During the first cycle (field increased to +8 kOe and then brought back to 1 kOe), a hysteresis of about 10% for samples A through D was noticed. If the samples are cooled in a field of 8 kOe, no similar hysteresis was observed. Subsequently, we cooled one sample (D) in nearly zero magnetic field (actually the residual field in the electromagnet was about 50 Oe) and studied its mag-

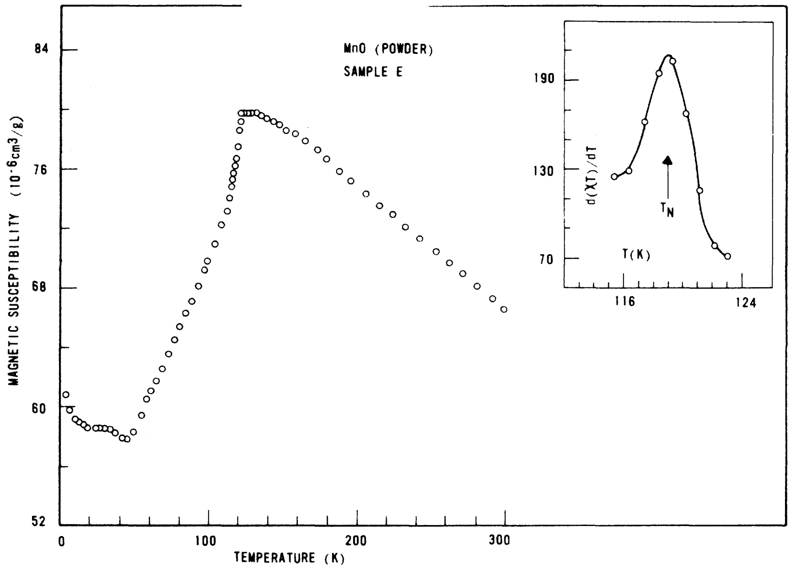

FIG. 2. The magnetic-susceptibility variation with temperature for a pure MnO powder sample (same as sample E in Fig. 1, but in the complete temperature range). The inset shows the method adopted for obtaining T_N.

netization behavior and results are shown in Fig. 4. The magnetization process has several distinct features. Significant hysteresis is observed during the first cycle. However, in subsequent cycles, the hysteresis loop is quite narrow and displaced (Fig. 5). This observation may be due to exchange anisotropy[20] induced at the ferrimagnetic-antiferromagnetic (Mn_3O_4–MnO) interfaces. We will return to these results later.

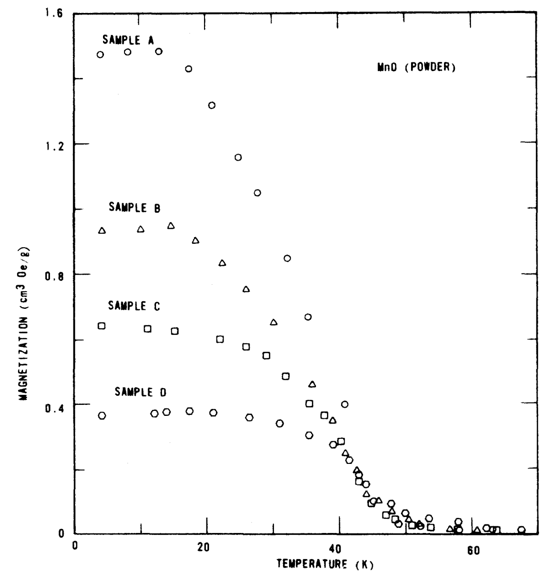

FIG. 3. The temperature variation of the zero-field magnetization for four MnO samples (Table I).

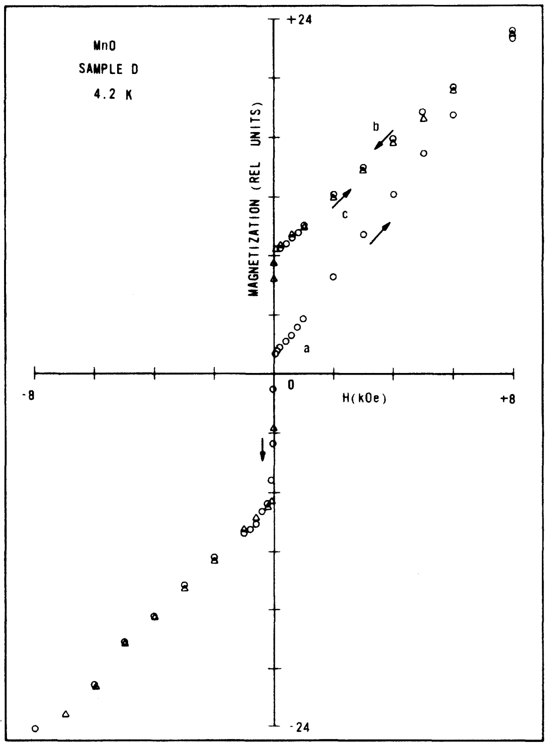

FIG. 4. Magnetic hysteresis obtained on cooling the MnO sample D to 4.2 K in nearly zero magnetic field. Triangles (Δ) refer to the data obtained after reaching −8 kOe. The starting point is denoted by *a*.

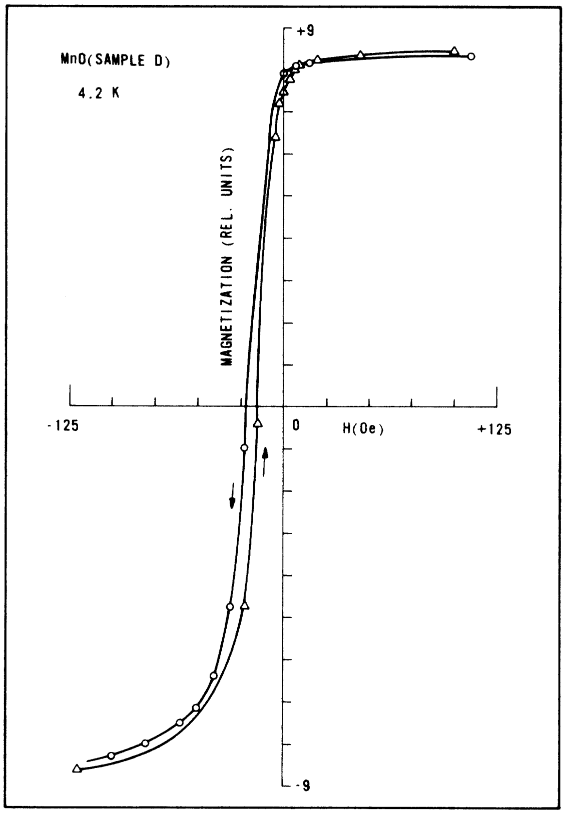

FIG. 5. Expanded view of the magnetic hysteresis (that shown in Fig. 4) at very low fields. Note the shifted hysteresis loop, away from the origin.

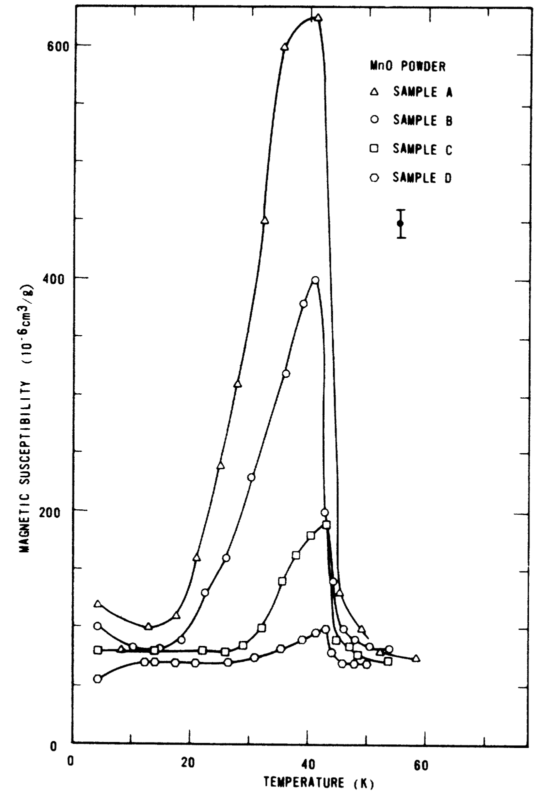

FIG. 6. The temperature variation of the magnetic susceptibility of Mn_3O_4 phase in MnO samples, derived by the method described in the text. The peaks occur near 43 K, the T_c for Mn_3O_4. The lines through the points are drawn for visual aid and clarity.

The magnetic susceptibility below 60 K has been evaluated by the following technique. An examination of M vs H curve of Fig. 4 suggests that the magnetization M approximately varies as $M = M_s + \chi_p H$, where χ_p is the susceptibility (in this case, $\chi_p \sim$ the sum of the susceptibilities of Mn_3O_4 and MnO, assuming negligible interaction between the two species). It follows that $(M/H) = (M_s/H) + \chi_p$. Therefore, a plot of (M/H) vs $(1/H)$ should yield a straight line with the slope M_s and χ_p as the intercept. It was seen that this plot is linear below 20 K and above 50 K (up to $H = 8$ kOe used in these measurements). The M_s values agreed perfectly with those shown in Fig. 3. For the 20–50-K range, where nonlinearity is present in these plots, the low-field side of the curve was chosen, where the slope yielded M_s values in agreement with those shown in Fig. 3. The important new information is in the variation of χ_p with temperature, shown in Fig. 6. The peak in χ_p occurs near 43 K, the T_c for Mn_3O_4. This is understandable since the variation of χ for pure MnO is relatively small ($\sim$20%) in the temperature range of 4.2–50 K. We believe that this is further confirmation of our suggestion that the impurity in MnO is Mn_3O_4. Powder x-ray analysis of all the samples was also carried out to detect Mn_3O_4. Several major lines characteristic of Mn_3O_4 (with sample E as a reference for pure MnO) were observed in samples A, B, C, and D using long scans (at least 16 h), with Cr K_α radiation.

In order to convert Mn_3O_4 to MnO present in our "MnO" samples, we attempted several experiments. In an initial experiment, an MnO crystal was placed in a quartz tube, evacuated to 10^{-5} Torr and sealed. The sample was then annealed for two days at 1353 K and quenched to room temperature. The magnetic properties were again measured. It was found that a reduction in the concentration of Mn_3O_4 did occur. Annealing another sample for four days produced further reduction. These results are consistent with the Mn–O phase diagram at high temperatures.[25] Following the work of Price and Wagner[26] who studied the diffusion of Mn in crystalline MnO, we then tried a different experiment to achieve a pure MnO crystal. In this experiment, a small amount of Mn was placed at one end of the quartz tube, whereas a

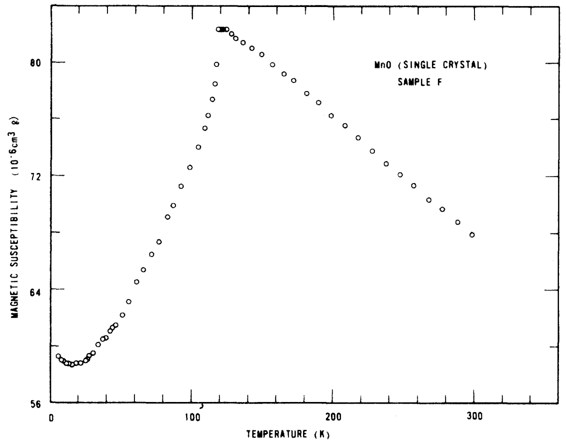

FIG. 7. The magnetic-susceptibility variation with temperature for an annealed MnO single crystal oriented randomly (sample F).

MnO single crystal (sample D) was placed at the other end and the tube was sealed under a vacuum of 10^{-5}Torr. The tube was then heated for about 200 h at 1293 K and quenched to room temperature. The magnetic susceptibility of the sample in the single-crystal form (sample F) was again measured after etching in dilute HCl and washing with H_2O and acetone, and the results for a random orientation are shown in Fig. 7. There was no hint of the remanent magnetization at 4.2 K or at higher temperatures. The M vs H data for this sample and sample E are shown in Fig. 8. From this and the comparison of the data of Figs. 2 and 7, it is clear that the results for samples E and F are quite similar, suggesting the complete absence of Mn_3O_4 after the annealing in Mn atmosphere. Although gravimetric[27] and electrical properties[28] of MnO for different levels of nonstoichiometry have been reported in the literature, to our knowledge this is the first time that a pure MnO single crystal has been obtained by the technique described above.

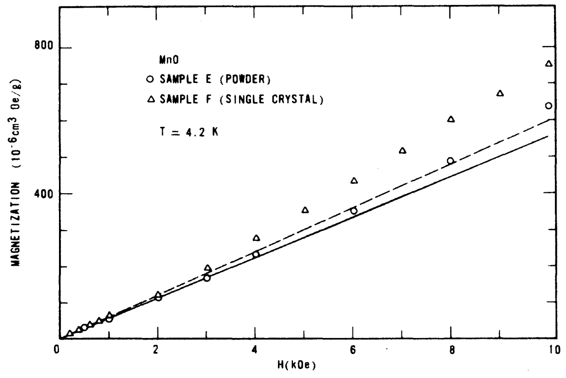

FIG. 8. The magnetic-field dependence of the magnetization for pure MnO samples (E and F). The straight lines (full for sample E and dotted for sample F) demonstrate the deviation at higher fields from the low-field behavior.

IV. DISCUSSION

From the data in Fig. 1, it is noted that below T_N, the minimum in the susceptibility for samples A through D occurs at different temperatures. There appears to be a direct correlation between the magnitude of Mn_3O_4 present in a sample and the temperature at which the minimum occurs. The approximate temperatures for the minimum are, respectively, 80, 75, 70, and 70 K for samples A, B, C, and D (Fig. 1). Now the magnetic susceptibility of Mn_3O_4 is expected to increase very rapidly as the temperature is lowered towards T_c (43 K), whereas χ for MnO follows the variation shown in Fig. 2. Therefore the above behavior of the shift in the minimum temperature with Mn_3O_4 concentration is easily understood if we make the reasonable assumption that the measured susceptibility is some combination of the relative susceptibilities of MnO and Mn_3O_4.

Next we consider the possible effects of the Mn_3O_4 impurity on the magnetic properties of MnO near and above T_N. From the data presented in Table I and Fig. 1, it follows that there is no systematic variation of the susceptibility or the Néel temperature with the concentration of Mn_3O_4. However, a more definite result of the effect of Mn_3O_4 impurity on χ and T_N is obtained by comparing the values for these parameters for sample F (with Mn_3O_4 impurity removed) with those for its parent sample D (with 2 at.% Mn_3O_4). This comparison (Table I) shows that the absolute values of χ and T_N, within the experimental uncertainties of $\pm 1\%$ and ± 0.5 K, respectively, in the absolute values,[24] are unaffected by about 2 at.% Mn_3O_4 impurity. To provide an explanation for this behavior, we follow similar line of reasoning as used in the preceding paragraph. Near room temperature, χ/g for Mn_3O_4 is smaller[19] than that for MnO. A simple calculation, assuming negligible interaction between the two phases, shows that a concentration of about 3 at.% Mn_3O_4 in MnO would actually lower the total susceptibility by about 1% (equal to the experimental uncertainty). Therefore, the impurity levels of few atomic percent are not detectable by the magnetic-susceptibility studies above T_N. The value of T_N should also be unaffected by a few atomic percent of Mn_3O_4 since χ for Mn_3O_4 is varying very slowly relative to that for MnO near the Néel temperature of MnO. The irregular variation of χ and T_N with the level of Mn_3O_4 impurity in the unannealed samples A through D (Table I) cannot, however, be understood on the basis of the above arguments. These irregularities perhaps reflect the way in which the Mn_3O_4 impurity is distributed in the MnO matrix in various samples.

At 4.2 K, in the ordered state of Mn_3O_4 and MnO, the observation of a displaced hysteresis loop (Fig. 5) suggests the presence of an interaction between the two phases. Such a displaced loop is usually attributed to the exchange anisotropy induced at ferromagnetic-antiferromagnetic interfaces when a sample is cooled in a magnetic field and the magnitude of the exchange anisotropy is given by the displaced area.[20] Such a displaced loop has also been observed in wustite (Fe_xO, $x = 0.945$)[29] and Co–CoO system.[30] There is, however, an important difference in the present observations in that the displaced loop is observed whether the sample is cooled in a magnetic field or in a nearly zero magnetic field. In the latter case, after the initial hysteresis in the first cycle, the displaced loop is observed in subsequent cycles (Fig. 4). This may in some way be related to the fact that T_c for the ferrimagnetic phase is less than T_N for the antiferromagnetic phase in the Mn_3O_4–MnO system, in contrast to the situation in the Co–CoO system. Additional studies are necessary to understand the observations presented here.

V. CONCLUDING REMARKS

Definite evidence for the presence of Mn_3O_4 in commercially available single crystals of MnO has been presented in this paper. We have also described a procedure for the conversion of the Mn_3O_4 impurity found in these crystals into MnO. The effect of even a few atomic percent of Mn_3O_4 impurity on the magnetic properties of MnO is very significant at low temperatures. A displaced hysteresis loop, observed at 4.2 K, is attributed to the exchange anisotropy induced at the ferrimagnetic-antiferromagnetic (Mn_3O_4–MnO) interfaces although additional studies are needed to explain all the observations. The effects of a few percent of Mn_3O_4 usually present in commercial crystals of MnO on other properties (such as optical[16,17] and elastic[6]) remain to be investigated. However, it is clear that care must be taken to characterize these samples before studies on such samples are undertaken.

In the near future, we hope to complete our studies on the principal susceptibilities of MnO, now that a pure single crystal of MnO is available. Then one can hope to improve upon the calculations of the exchange and anisotropy parameters for MnO based on the powder susceptibilities.[13] Plans are also underway to study the details of the kinetics of Mn_3O_4–MnO conversions under different atmospheres, temperatures, and durations.

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[1] See, e.g., the recent review by B. H. Brandow, Adv. Phys. 26, 651 (1977).

[2] R. W. Millar, J. Am. Chem. Soc. 50, 1875 (1928).

[3] H. Bizette, C. Squire, and B. Tsai, C. R. Acad. Sci. 207, 449 (1938).

[4] M. Foëx, C. R. Acad. Sci. 227, 193 (1948).

[5] C. G. Shull and J. S. Smart, Phys. Rev. 76, 1256 (1949); C. G. Shull, W. A. Strauser, and E. O. Wollan, *ibid.* 83, 333 (1951); W. L. Roth, *ibid.* 110, 1333 (1958).

[6] D. Bloch, P. Charbit, and R. Georges, C. R. Acad. Sci. 266, 430 (1968); B. Morosin, Phys. Rev. B 1, 236 (1970).

[7] P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. 36, 52 (1976); P. Bak and D. Mukamel Phys. Rev. B 13, 5086 (1976).

[8] S. A. Brazovskii, I. E. Dzyaloshinskii, and B. G. Kukharenko, Sov. Phys. JETP 43, 1178 (1976).

[9] M. F. Cracknell and R. G. Evans, Solid State Commun. 8, 359 (1970).

[10] D. Bloch, R. Maury, C. Vetter, and W. B. Yelon, Phys. Lett. A 49, 354 (1974).

[11] D. Seino, S. Miyahara, and Y. Noro, Phys. Lett. A 44, 35 (1973).

[12] C. F. Van Doorn and P. de V. DuPlessis, Phys. Lett. A 66, 141 (1978).

[13] D. Bloch, J. L. Feron, R. Georges, and I. S. Jacobs, J. Appl. Phys. 38, 1474 (1967); D. Bloch, R. Georges, and I. S. Jacobs, J. Phys. (Paris) 31, 589 (1970).

[14] J. J. Wanewicz, R. F. Heidelberg, and A. H. Luxem, J. Phys. Chem. 65, 615 (1961).

[15] T. R. McGuire and R. J. Happel, Jr., J. Phys. Radium 20, 424 (1959); T. R. McGuire and W. A. Crapo, J. Appl. Phys. 33, 1291 (1962).

[16] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 395 (1975).

[17] L. Messick, W. C. Walker, and R. Glosser, Phys. Rev. B 6, 3941 (1972).

[18] I. S. Jacobs, J. Phys. Chem. Solids 11, 1 (1959).

[19] A. S. Borovick-Ramanov and M. P. Orlova, Sov. Phys. JETP 5, 1023 (1957).

[20] J. S. Kouvel, J. Phys. Chem. Solids 24, 795 (1963).

[21] M. S. Seehra and M. S. Jagadeesh, Phys. Rev. B 20, 3897 (1979).

[22] M. S. Seehra and P. Silinsky, Solid State Commun. 31, 183 (1979).

[23] E. E. Bragg and M. S. Seehra, Phys. Rev. B 7, 4197 (1973).

[24] Note that the sample temperatures were measured with thermocouples, not in direct contact with the sample, but about 0.5 cm away from the sample. Care was taken to see that temperatures were stable to better then 0.1 K for at least 5 min before each datum is recorded. This was substantiated further by the reproducibility of the entire data set on repeating the whole cycle. The absolute accuracy of T_N's is estimated to be ±0.5 K where as the relative accuracy of the temperature measurements is about 0.1 K. For additional details see Ref. 21.

[25] A. Z. Hed and D. S. Tannhauser, J. Electrochem. Soc. 114, 314 (1967).

[26] J. B. Price and J. B. Wagner, J. Electrochem. Soc. 117, 242 (1970).

[27] I. Bransky and N. M. Tallan, J. Electrochem. Soc. 118, 788 (1972).

[28] A. Z. Hed and D. S. Tannhauser, J. Chem. Phys. 47, 2090 (1967).

[29] W. L. Roth, J. Appl. Phys. 30, 303S (1959).

[30] W. H. Meiklejohn and C. P. Bean, Phys. Rev. 102, 1413 (1956).