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Spin-glass transition in MnO

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What could possibly be new in MnO 46 years after the discovery of its antiferromagnetic transition?: a spin-glass transition in the (25—50)-K temperature range. The susceptibility of MnO powders obtained by various treatments (MnO aged 30 years in ambient atmosphere, MnO_2 reduced at 500 and 1000 °C in hydrogen, and MnO heated in air at 500 °C) was measured in low dc and ac magnetic fields and in a high dc magnetic field. The spin-glass behavior is linked to a slight off-stoichiometry: MnO_{1+x} with $x \leq 0.01$. It is not believed that the susceptibility peak arises from a mixture of MnO and Mn_3O_4. This conclusion is based on the shape of the susceptibility curves at both the spin-glass temperature (T_{SG}) and the Néel temperature as well as on the various T_{SG} values which differ from the ferrimagnetic transition of Mn_3O_4. It is more likely that the spin-glass interaction occurs either between Mn_3O_4-like clusters or between defects typical in MnO such as an interstitial Mn surrounded by four Mn vacancies.

I. INTRODUCTION

This investigation started when it was decided to use MnO in order to calibrate a magnetometer[1] using a superconducting quantum-interference device (SQUID). The choice of MnO was based on the fact that both the temperature dependence of its susceptibility and the antiferromagnetic transition at $T_N \simeq 120$ K have been well known[2] for a long time. The calibration was performed using an MnO powder which had aged for 30 years in ambient atmosphere, which led to the discovery of a spin-glass-type transition at 50 K. In order to elucidate the causes for this behavior, it was then decided to study MnO powders prepared in various ways.

II. EXPERIMENTAL PROCEDURE

The magnetic susceptibility of the various MnO powders was measured in three different apparatuses. The low-field ($H = 1$ Oe) dc susceptibility (χ) was measured in a SQUID magnetometer[1] while the low-field ac χ was obtained at 10 kHz with $H_{ac} = 4$ Oe in a push-rod susceptibility holder.[3] The high-field dc susceptibility was measured using the Faraday method.[4]

III. EXPERIMENTAL RESULTS AND DISCUSSION

The first evidence for a spin-glass transition using the SQUID magnetometer is shown in Fig. 1(a) for an MnO powder which was aged 30 years in ambient atmosphere. The two heating runs were conducted by first cooling the sample in zero field to 4.2 K, then applying the 1-Oe measuring field and measuring the susceptibility with increasing temperature, which results in a typical spin-glass susceptibility cusp at $T_{SG} \simeq 50$ K. Further evidence for a spin-glass-type transition is given in Fig. 1(a) by the irreversible behavior shown upon cooling the sample in a 1-Oe magnetic field. Since the zero-field-cooled curves of Fig. 1(a) represent the reversible part of the magnetization, the same cusp should appear in an ac susceptibility measurement as shown in Fig. 1(b) by the $H_{dc} = 0$ curve. It is also apparent from Fig. 1(b) that as is typical in most spin-glasses, the cusp becomes rounded off when a dc magnetic field is superimposed on the measuring ac field. At the higher temperatures, both dc [Fig. 1(a)] and ac [Fig. 1(b)] susceptibilities tend towards the high-temperature susceptibility reported for antiferromagnetic MnO.[2] The overall behavior of the susceptibility is best seen in Fig. 2 which displays the temperature dependence of the high-field dc susceptibility. The antiferromagnetic transition at $\simeq 120$ K is clearly visible in addition to the spin-glass transition which in this case is indicated by the inflection point at $\simeq 45$ K which corresponds to the susceptibility peaks of Figs. 1(a) and 1(b). There are, however, subtle differences in the susceptibility break at

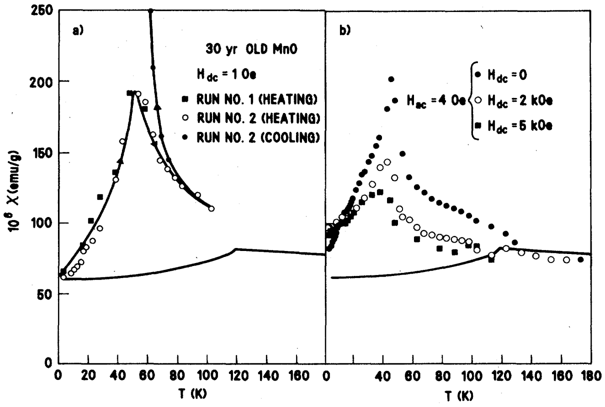

FIG. 1. (a) dc susceptibility as a function of temperature for the 30-year-old MnO. (b) ac susceptibility as a function of temperature and applied dc magnetic field. The lowest solid curve shows the expected susceptibility (Ref. 2) for antiferromagnetic MnO.

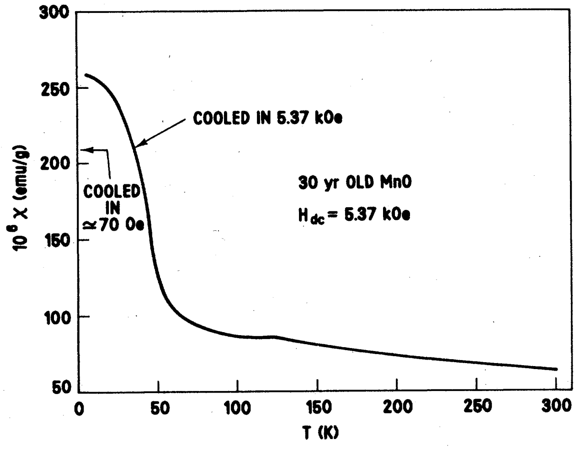

FIG. 2. High-field dc susceptibility as a function of temperature for the 30-year-old MnO. The arrow indicates the susceptibility obtained by cooling in the remnant field of the magnet.

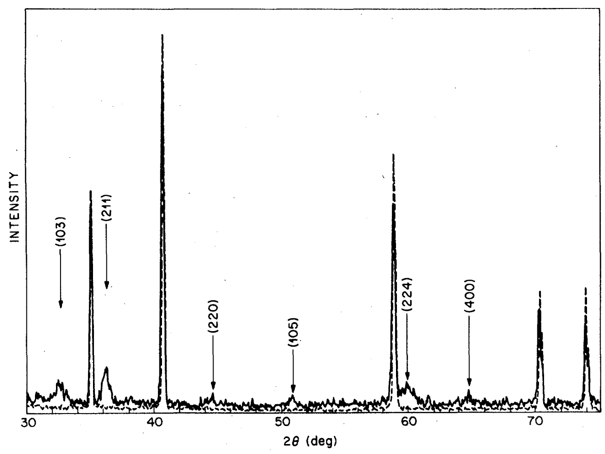

FIG. 3. X-ray diffractometer patterns for fully reduced MnO powder (obtained by heating MnO_2 in H_2 at 1000 °C) shown as the dashed line and for the same powder heated 45 min at 500 °C in air (solid line). The indices with arrows indicate the diffraction peaks for Hausmannite (Mn_3O_4).

$T_N \simeq 120$ K between various MnO powders which will be discussed later on. Another characteristic of spin-glasses is reflected in the sensitivity of the susceptibility to the cooling field (Fig. 2). Therefore, to summarize Figs. 1 and 2, the 30-year-old powder is clearly displaying a spin-glass transition in addition to the well-known antiferromagnetic transition at 120 K. The investigation of this anomaly will proceed in two directions: first, by characterizing the 30-year-old powder, and second, by attempting to obtain a similar behavior in powders subjected to well-defined heat treatments.

One may be tempted to attribute the spin-glass phase to some impurity in the sample. The 30-year-old powder has a dark green (blackish-green) appearance while fully reduced MnO powder (which as will be discussed later is obtained by reducing MnO_2 at 1000 °C in hydrogen) has a light bright green color. This would suggest the presence of some higher oxidation state of Mn (Mn^{3+}). Otherwise, an x-ray fluorescence analysis of the powder failed to reveal any impurity. The x-ray diffraction pattern for this powder is essentially identical to that published in the literature for MnO. More precisely, the x-ray pattern is similar to that shown in Fig. 3 for an MnO powder containing some Mn_3O_4 (of course without the Mn_3O_4 lines), and it is clear from Fig. 3 that the MnO lines for that powder are indistinguishable from that of fully reduced MnO. As shown in Table I, the maximum difference between the lattice parameters of the 30-year-old powder and fully reduced MnO is extremely small and within experimetal error. Furthermore, measurements of the weight loss occurring after annealing the 30-year-old powder for 3 h at 1000 °C in hydrogen, which yields fully reduced MnO, give an estimate of the maximum off-stoichiometry which corresponds to $MnO_{1.01}$. Although impurities have been ruled out by x-ray fluorescence analysis, the possibility of an impurity effect was further investigated by measuring the mineral manganosite which is known to contain 3.4—4.9 wt. % of ZnO and 0.23—0.26 wt. % of FeO and/or Fe_2O_3. An x-ray fluorescence analysis of the mineral revealed 3.5 wt. % ZnO but could not detect the Fe because the fluorescence of such a small Fe concentration is hidden under the strong neighboring Mn fluorescence. At any rate, as shown in Fig. 4, despite the impurities present there is no spin-glass transition and only an antiferromagnetic transition around 120 K. The susceptibility data are fitted approximately by the solid curve which was obtained by adding to the susceptibility of pure[2] MnO a temperature-independent susceptibility term which is reasonable for the amount of FeO and/or Fe_2O_3 present. Further proof that the spin-glass phase is not the result of some impurity (other than Fe or Zn) will be given below by comparing the 30-year-old MnO

TABLE I. Lattice parameter (a) for various MnO powders.

Powder treatment	a (Å)	$\Delta a/a$[a]
MnO_2 reduced for 3 h in H_2 at 1000 °C → MnO	4.434±0.004	0
MnO 30-year-old powder	4.435±0.003	2×10^{-4}
MnO_2 reduced for 3 h in H_2 at 500 °C	4.436±0.004	3×10^{-4}
MnO heated 18 min in air at 500 °C	4.436±0.004	4×10^{-4}
MnO heated 45 min in air at 500 °C	4.436±0.003	5×10^{-4}

[a] Δa is the maximum difference in lattice parameters between an off-stoichiometric MnO powder and the fully stoichiometric MnO obtained by reduction at 1000 °C of MnO_2.

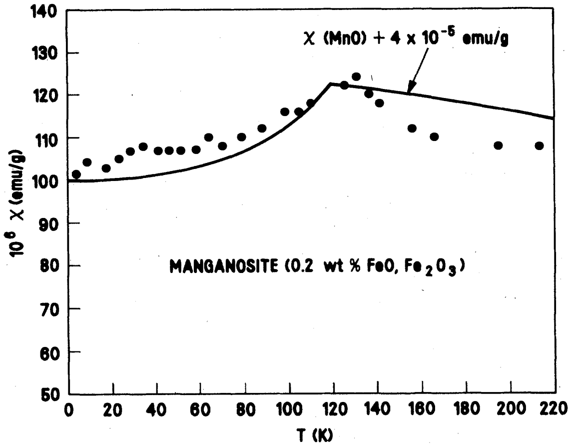

FIG. 4. ac susceptibility as a function of temperature for the mineral manganosite (solid circles). The solid curve was calculated by adding a constant susceptibility to that published in Ref. 2 for pure MnO.

powder with MnO_2 powder reduced at 500 °C. Having established that the spin-glass transition observed in the 30-year-old MnO powder is not an impurity effect, we will attempt to obtain a similar behavior by well-characterized heat treatments in order to understand the origin of this effect.

First, MnO was prepared by reducing pure MnO_2 powder by heating for 2 h at 500 °C in hydrogen. As shown in the top of Fig. 5, besides the antiferromagnetic transition at 120 K, this powder displays a clear spin-glass cusp at 40 K which is quite similar to that observed in Figs. 1(a) and 1(b) for the 30-year-old in MnO powder. Further reduction of the MnO_2 powder at the same temperature yields the data shown in the bottom of Fig. 5. It is apparent from Fig. 5 (bottom) that the spin-glass transition is still present but comparison with Fig. 5 (top) shows that the susceptibility cusp is about half and T_{SG} has decreased from 40 to 30 K. This would suggest that complete reduction would eliminate the spin-glass transition. However, despite the fact that the MnO_2 powder reduced for 3 h in hydrogen is still blackish-green (i.e., contains some Mn^{3+}) it is clear from Table I that it is essentially MnO. Indeed, the maximum difference in lattice parameter with stoichiometric MnO is within experimental error. Furthermore, weighing the starting MnO_2 powder and the powder after heat treatment establishes that the maximum off-stoichiometry would correspond to $MnO_{1.01}$. The spin-glass behavior is further established by the high-field dc susceptibility data shown in Fig. 6. As in all spin-glasses one observes a pronounced difference in the susceptibility below $T_{SG} \simeq 30$ K depending on whether one cools or heats in a dc magnetic field. On the other hand, the antiferromagnetic transition at 120 K is as expected independent on the way the data are obtained. It is also clear that the high-field dc data shown in Fig. 6 for MnO_2 reduced 3 h at 500 °C are qualitatively similar to those shown in Fig. 2 for the 30-year-old MnO powder. This result adds further support to the previous statement that the spin-glass transition is not the result of an impurity

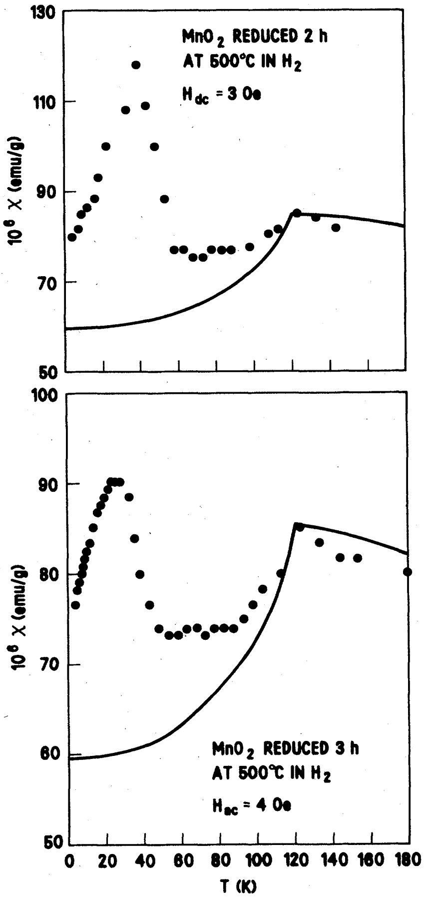

FIG. 5. Top: dc susceptibility as a function of temperature for MnO_2 heated 2 h in hydrogen at 500 °C. Bottom: ac susceptibility as a function of temperature for MnO_2 heated 3 h in hydrogen at 500 °C. The solid curve shows the susceptibility for MnO of Ref. 2.

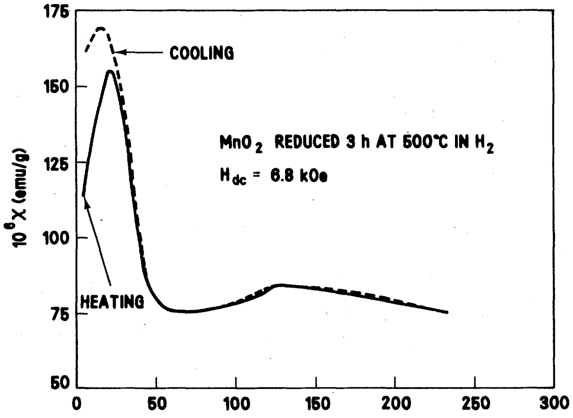

FIG. 6. High-field dc susceptibility as a function of temperature for MnO_2 reduced 3 h at 500 °C.

effect. Indeed, reducing MnO_2 powder at 500 °C yields a spin-glass transition similar to that observed in the 30-year-old powder, while reducing the same MnO_2 powder at 1000 °C eliminates the spin-glass transition and leaves only the classical antiferromagnetic transition (Fig. 7) reported[2] for pure stoichiometric MnO. A better comparison between these powders and fully reduced MnO is made in Fig. 7. The fully reduced stoichiometric MnO powder was obtained by heating MnO_2 for 3 h in hydrogen at 1000 °C which yielded a light bright green powder. The susceptibility curve shown in Fig. 7 for this powder is essentially identical to that shown in Ref. 2 with a sharp drop below $T_N \simeq 120$ K characteristic of a first-order transition. On the other hand, the 30-year-old MnO and the MnO_2 reduced at 500 °C, which both display a spin-glass transition, do not exhibit a sharp drop at T_N; as a matter of fact, the more pronounced the spin-glass transition, i.e., the greater the increase in χ at low temperatures, the greater the smearing of the antiferromagnetic transtion at $\simeq 120$ K. This would suggest that the spin-glass transition does not occur as a result of a second phase such as Mn_3O_4 embedded in otherwise stoichiometric MnO since such a structure should yield a spin-glass transition along with a sharp antiferromagnetic transition at 120 K. The possibility of Mn_3O_4 being responsible for the susceptibility cusp will be further ruled out by the experiments described below.

The fact that the presence of a spin-glass transition leads to a smearing of the antiferromagnetic transition would suggest that both transitions occur in the same phase. In other words, as the temperature is lowered, it is the same Mn spins which undergo a paramagnetic to antiferromagnetic transition at 120 K that undergo an antiferromagnetic to spin-glass state at lower temperatures. This is synonymous to saying that slightly off-stoichiometric MnO is a "reentrant antiferromagnet" analogous to the reentrant ferromagnet[5] $Eu_{1-x}Sr_xS$ for the correct values of x.

Since the spin-glass transition was attributed to the presence of Mn^{3+} (i.e., $MnO_{1.01}$) either by an incomplete reduction of MnO_2 powder at 500 °C or by a slight oxidation in the 30-year-old MnO powder, we will now attempt to simulate the latter effect by partially oxidizing the fully reduced MnO powder. Indeed, if the MnO powder obtained by fully reducing MnO_2 for 3 h at 1000 °C in hydrogen (Fig. 7) is heated for 3 h in air at 1000 °C, it is fully converted to Mn_3O_4 as shown by x-ray diffraction and by the ferrimagnetic transition at 42 K (Fig. 8) which is in excellent agreement with previous results.[6] The oxygen-rich MnO will therefore be obtained by heating fully reduced MnO at 500 °C in air for a short time. The susceptibility measurements on a sample heated for 18 min in air are shown in the top of Fig. 9. The susceptibility for the starting MnO powder is shown as solid circles for the ac measurement which are in excellent agreement within experimental error with the high-field dc measurements shown as open circles (these open circles are the same data as shown in Fig. 7 for MnO_2 reduced at 1000 °C). It is clear from Fig. 9 (top) that this powder displays a susceptibility cusp at $\simeq 48$ K fairly similar to those previously discussed although the powder is essentially MnO. Indeed, x-ray diffraction failed to reveal any Mn_3O_4 peak and as shown in Table I the maximum difference in lattice parameter with stoichiometric MnO is within experimental error. Nevertheless, since the ferrimagnetic Curie point (42 K) of Mn_3O_4 is close to the temperature of maximum susceptibility, we will attempt to fit the cusp by assuming a mixture of Mn_3O_4 and MnO. The solid curve shown in Fig. 9 (top) was calculated by weighting the susceptibility of MnO and of Mn_3O_4 (Fig. 8) so as to fit the maximum susceptibility value which corresponds to 0.59 wt. % of Mn_3O_4. Such a small amount of Mn_3O_4 is plausible since, based on the magnitude of Mn_3O_4 diffraction peaks shown in Fig. 3 for 11.6 wt. % Mn_3O_4, it would not be detectable by x-ray diffraction. It is, however, clear from Fig. 9 (top) that the solid curve is a poor approximation of the susceptibility cusp. Further oxidation of the MnO powder (45 min) causes the appearance of Mn_3O_4 diffraction peaks (Fig. 3). Taking intensity ratios between MnO and Mn_3O_4 diffraction peaks yields a crude estimate

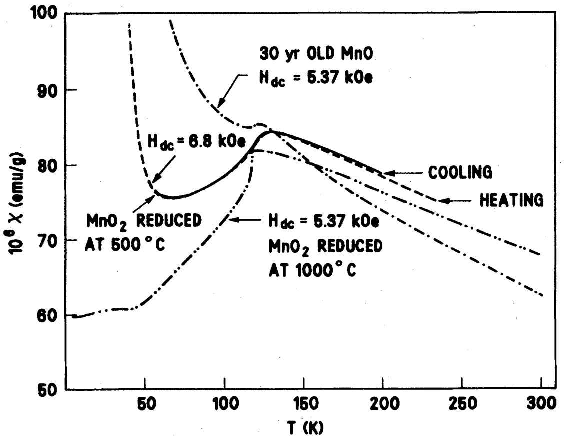

FIG. 7. High-field dc susceptibility as a function of temperature for the 30-year-old MnO powder and for MnO_2 reduced 3 h in hydrogen at 500 and 1000 °C (stoichiometric MnO).

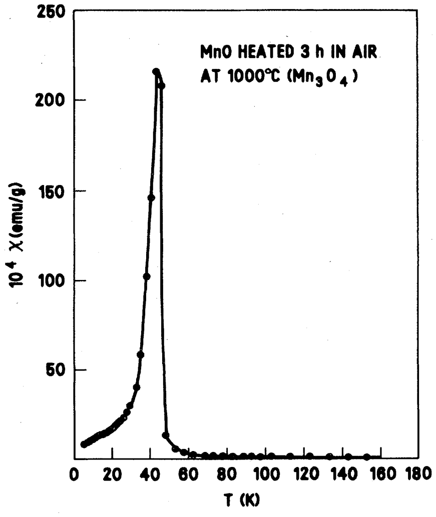

FIG. 8. ac susceptibility of Mn_3O_4 as a function of temperature

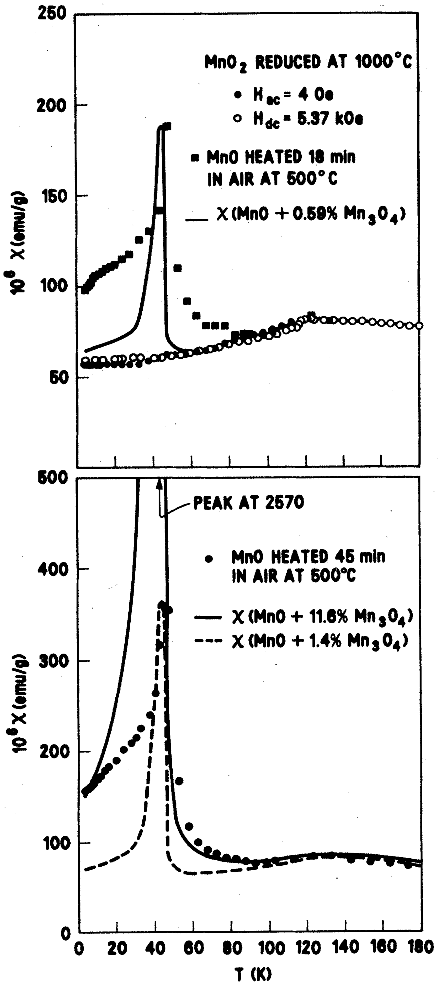

FIG. 9. Top: ac susceptibility (solid squares) for MnO heated for 18 min in air. The susceptibility for the starting MnO powder (MnO_2 reduced at 1000 °C) is shown as solid cirlces (ac) and open circles (dc). Bottom: ac susceptibility (solid circles) for MnO heated for 45 min in air. The solid and dashed curves are calculated as described in text.

of about 11.6 wt. % Mn_3O_4. Again as shown in Table I the lattice parameter of the heat-treated MnO is within experimental error equal to that of stoichiometric MnO. The susceptibility data for this mixed MnO-Mn_3O_4 sample are shown at the bottom of Fig. 9. If one attempts to fit the maximum value of the susceptibility as above [dashed curve in Fig. 9 (bottom)] this would correspond to 1.4 wt. % Mn_3O_4 in total disagreement with the estimate from x-ray intensity. If, on the other hand, one calculates the susceptibility by using the 11.6 wt. % Mn_3O_4 estimated by x-ray intensity [solid curve in Fig. 9 (bottom)], the calculated susceptibility is almost an order of magnitude higher than the experimental one at 45 K. It is therefore clear from Fig. 9 that the susceptibility peak at $\simeq$45 K cannot be explained by a mixture of MnO and Mn_3O_4. One could, however, object that the Mn_3O_4 present in these various MnO powders cannot be described by the susceptibility shown in Fig. 8 for bulk Mn_3O_4. For example, the Mn_3O_4 could be present in the form of microscopic superparamagnetic clusters. Even if this were the case we would argue that the susceptibility cusps arise from a spin-glass interaction between the clusters based on the fact that the susceptibility peak occurs at various temperatures (from 50 to 30 K depending on heat treatment), usually distinct from the ferrimagnetic transition of Mn_3O_4 at 42 K.

This is different from electron-spin-resonance experiments[7] and magnetic studies[8,9] of nonstoichiometric MnO resulting from Mn_3O_4 inclusions (2—8 mol %) detectable by x-ray diffraction which display the Néel transition at 118 K and the ferrimagnetic transition at 42 K.

IV. CONCLUSIONS

A spin-glass transition has been observed in slightly off-stoichiometric MnO ($MnO_{1.01}$ at the most). The spin-glass transition exists in incompletely reduced MnO_2 powder or slightly oxidized MnO powder and is absent in fully reduced MnO. The spin-glass interaction occurs either between Mn_3O_4-like clusters or between defects typical in MnO such as an interstitial Mn surrounded by 4 Mn vacancies. It has been argued recently[10] that the defect structure changes as one goes from the Mn-MnO to the MnO-Mn_3O_4 boundary. Since the present samples were all in the latter domain, we intend to study in the future samples next to the Mn-MnO boundary (i.e., MnO_{1-x}) in order to see whether the spin-glass transition will still be present.

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