Magnetic susceptibility, specific heat and dielectric constant of hexagonal YMnO$_3$, LuMnO$_3$ and ScMnO$_3$

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We report the magnetic susceptibility, specific heat and dielectric constant on high purity polycrystalline samples of three hexagonal manganites: YMnO$_3$, LuMnO$_3$ and ScMnO$_3$. These materials can exhibit a ferroelectric transition at very high temperatures ($T_{FE} > 700$ K). At lower temperatures there is magnetic ordering of the frustrated Mn$^{3+}$ spins ($S=2$) on a triangular Mn lattice (YMnO$_3$: $T_N = 71$ K; LuMnO$_3$: $T_N = 90$ K and ScMnO$_3$: $T_N = 130$ K). The transition is characterized by a sharp kink in the magnetic susceptibility at $T_N$ below which it continues to increase due to the frustration on the triangular lattice. The specific heat shows one clear continuous phase transition at $T_N$, which is independent of external magnetic field up to 9 T with an entropy content as expected for Mn$^{3+}$ ions. The temperature dependent dielectric constant displays a distinct anomaly at $T_N$. 
I. INTRODUCTION

Rare-earth manganites of the perovskite-type structure REMnO$_3$ have been discovered in the 1950s. Materials with small ionic radius (RE = Ho, Er, Tm, Yb, Lu, Y and Sc) crystallize in the hexagonal structure [S.G. $P6_3cm$] while the compounds with larger ionic radius (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy) are orthorhombic [S.G.$Pnma$] [1]. The orthorhombic compounds (S.G. $Pnma$) form the basis for the CMR materials and they have been studied widely in the recent years. Unlike their orthorhombic counterparts, investigations in hexagonal REMnO$_3$ compounds are few despite their interesting properties. Systems belonging to the hexagonal class undergo a ferroelectric transition far above the ordering of Mn$^{3+}$ spins. Such magnetic ordering occurs in both structures, however, ferroelectricity is possible only for the hexagonal phase which has the noncentrosymmetric phase group $P6_3cm$. Although hexagonal manganites have been studied for many years [2–5], very recently there has been a resurgence of interest in these materials [6–8]. Most hexagonal REMnO$_3$ compounds can exhibit two transitions, i.e., a very high temperature ($T_{FE} \approx 900$ K) ferroelectric distortion and a low temperature ($\approx 100$ K) magnetic ordering. The development of two order parameters is a rarity in oxides [9] and opens the possibility for electric-magnetic interactions and ”tuning” with electric and magnetic fields.

Current efforts have focused on the magnetic transition and refining the magnetic structure [2–4, 10]. These investigations have been complicated by the formation of a ferromagnetic impurity phase, Mn$_3$O$_4$, with a Curie temperature $T_C \simeq 43$ K. Amounts of order of 0.5 at.\% of this phase are found in most samples reported to date [2–4, 11], causing significant anomalies in the bulk properties. For example, the true REMnO$_3$ antiferromagnetic transition is masked by the ferromagnetic signal in the susceptibility and the specific heat may exhibit a second strongly magnetic field dependent peak around 40 K with a tiny entropy content.

In order to examine the intrinsic magnetic transition, we have developed a preparation technique for fabrication of pure samples (impurity content less then 0.1 at.\%) of YMnO$_3$, LuMnO$_3$ and ScMnO$_3$. We have measured the magnetic susceptibility ($\chi$) up to 400 K in
different external fields. Specific heat ($C_p$) and its field dependence were also determined. Using a two Debye-temperature model we can deduce the excess $\Delta C_p$ and the magnetic entropy. Finally, we have measured the dielectric constant ($\epsilon$). Our results show that there is a single antiferromagnetic transition at $T_N$ in each of these compounds. However, there appears a continuous increase in $\chi(T)$ and a broad low $T$ maximum ($\approx 50$ K) in $\Delta C_p/T$ with significant entropy as the temperature is reduced. We attribute these anomalous features at $T < T_N$ to the frustration of Mn$^{3+}$ spins on a triangular lattice. From our measurements of the dielectric response of our high purity samples we find a more enhanced "$S$"-shaped curve than the one reported in a previous investigation [12]. This signature of $T_N$ in the dielectric susceptibility at $T_N \ll T_{FE}$ we believe is caused by a small change in the ferroelectric domain wall mobility and not by a direct coupling between the magnetic and ferroelectric order parameter.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The samples investigated were prepared by the solid-state reaction technique at ambient pressure. Cation oxides of $Y_2O_3$, $Lu_2O_3$, $Sc_2O_3$ (99.99%) and $MnO_2$ (99.99%), obtained from Alpha Aesar [13], were mixed in a 1:2 molar ratio to achieve the stoichiometry of hexagonal $LnMnO_3$. The mixture was well ground and calcinated in $O_2$-flow at 1100$^0$C for 24h. To ensure better homogeneity the mixtures were ground again, compacted into small pellets and reheated in air at 1400$^0$C for 48 h for YMnO$_3$ and LuMnO$_3$; and at 900$^0$C in flowing $O_2$ for ScMnO$_3$. It is only when this high-temperature "reheating" is done for YMnO$_3$ and LuMnO$_3$, and the exact procedures given in ref. [14] are followed for ScMnO$_3$ that we obtain impurity-free samples. This optimum procedure unfortunately depends slightly on the starting materials but the magnetic and structural properties of these compounds seem not to be sensitive to the $O_2$ content. We may have a small $\delta$ missing/exces in the oxygen stoichiometry such as REMnO$_{3+\delta}$.

The powder x-ray diffraction data on all three compounds show that the polycrystalline
samples have the correct hexagonal structure without any trace of impurity phases. The lattice parameters found for each compound are in agreement with previous reports [2,13]. The radius of the pellets is 1.5 mm and their thickness varies from 0.5 mm to 0.8 mm.

Dc-susceptibility ($\chi$) was measured in a Quantum Design magnetometer (MPMS 5S) for each sample using two fields, 0.1 T and 2 T in the temperature range from 1.8 to 400 K. Heat-capacity measurements were performed using a Quantum Design PPMS system in the range from 1.8 to 250 K and in fields up to 9 T. A relaxation technique was used with a resolution of 2% and an accuracy better than 5%. All samples showed only one sharp anomaly in the specific heat at $T_N$ without any additional peaks that could be ascribed to an impurity phase. Comparing with the specific heat of the most common impurity (Mn$_3$O$_4$) this leads to an estimation of less than 0.05% of this impurity. We also estimated the amount of second phase in all samples by measuring magnetization in different fields, which leads to even lower amounts. Finally we measured the dielectric constant $\epsilon$ as function of the temperature using a capacitance bridge operating at a frequency of 1 MHz.

III. SUSCEPTIBILITY

Magnetic susceptibility measurements on the hexagonal compounds previously investigated failed to show any clear anomaly at $T_N$ in the $\chi$ versus $T$ curve. In 1, 2 and 3 we show the results on our high purity samples. The anomaly at $T_N$ is evident from the graphs. Reciprocal susceptibilities are also shown as an inset of these figures.

As expected for triangular antiferromagnets the susceptibility at the lowest temperature ($T < T_N$) does not decrease to 2/3 of its value at $T_N$ as for the classical two-sublattice case. From the earliest neutron diffraction combined with group theory arguments for this hexagonal lattice, Berthaut et al. [15] concluded that the Mn magnetic moments are directed in the basal plane and are oriented with angles of 120° with respect to each other. If the field is perpendicular to the magnetic plane all spins will be canted out from the plane with a small angle $\delta$ in the direction of the applied field. For this field direction the zero-
temperature susceptibility will be equal to $\chi(T_N)$. A simple calculation with classical spins arranged with 120° angles, shows that $\chi(T = 0)$ is at least $\chi(T_N)$ for all directions of the field in the basal plane. A detailed calculation will be carried out for this intriguing behavior.

The insets of the figures 1-3 exhibit the reciprocal susceptibility versus temperature. By fitting with a Curie-Weiss law in the temperature range from 300 to 400 K the values of the effective Mn moments ($\mu_{eff}$) and the paramagnetic Curie temperatures ($\theta_{CW}$) could be obtained. Collects these parameters together with $T_N$, taken as the temperature where the kink in $\chi$ versus $T$ occurs.

Because of the large values of $\theta_{CW}$ the temperature range for the fits (300 K - 400 K) is still too low. This explains the slight discrepancies between the obtained effective moments and the expected value of the $Mn^{3+}(4.9\mu_B)$. Also the absolute values of $\theta_{CW}$ are much larger then the ordering temperature $T_N$. Ramirez defined the ratio between these parameters as the measure of the geometrical frustration of the antiferromagnetic system. For our in-plane triangular lattice these value appears to be of order 5 which puts our hexagonal system in the class of moderately frustrated systems.

Note that a ferromagnetic impurity (Mn$_3$O$_4$) content of less then 0.05% will be immediately visible from the susceptibility measurements in two fields (not shown), e.g. 0.1 and 2 T. Our samples do not show any sign of the presence of Mn$_3$O$_4$ meaning that its abundance is less then 100 ppm.

IV. SPECIFIC HEAT

The results of the specific heat measurements for all three compounds in 0 and 9 T magnetic fields are shown in the insets of the 4, 5 and 6 together with the estimates for their lattice contribution (dash lines). The lattice specific heat was estimated using two Debye functions for the "heavy"(Mn+RE) and "light"(O$_2$) elements in our compounds. The fits were carried out considering the specific heat at temperatures above 1.5 times $T_N$. We found reasonable values for the Debye temperatures, i.e., $\theta_D("light") \approx 780$ K - 800 K.
and $\theta_D$ ("heavy") $\approx 350$ K - 420 K. Subtraction of this estimation of the lattice specific heat provides us the (excess) magnetic contribution of the system. These $\Delta C_p$ are shown as $\Delta C_p/T$ versus T curves in 4, 5 and 6 (left y-axis). On the right ordinate we plot the entropy computed from the integral. All samples exhibit sharp anomalies at the corresponding transition temperature indicating the onset of antiferromagnetic order. Up to an applied field of 9 T the specific heat is independent of the field. Contrary to previous work [8] we could not detect a second lower temperature anomaly, which becomes visible when the sample is contaminated by more than 0.5% of impurity ($\text{Mn}_3\text{O}_4$). The resulting entropy is in excellent agreement with that expected for a $\text{Mn}^{3+}$ ion ($S=2$).

$$\Delta S = R \cdot \ln(2S + 1) = 13.38 \text{ J/mol} \cdot \text{K}$$

In the literature [8,11] discrepancies between the deduced and expected entropy up to a factor of 10 have been reported due to an inaccurate estimate of the lattice contribution. Our analysis gives values for $\Delta S$ of at least 90% of the expected one. Note that the magnitude of $\Delta C_p$ at $T_N$ is approximately the same for all three compounds (18 J/mol K).

Furthermore, there is an interesting anomaly ("bump") at low T ($\approx 50$ K) in the excess specific heat ($\Delta C_p/T$). The amount of entropy removed directly at $T_N$ is less than half of the total and this relative amount decreases going from Y via Lu to Sc. The physical cause of this "bump" in $\Delta C_p/T$ and the corresponding entropy involved is related, in our opinion, to the frustrated magnetism. Here it seems that there are still spin degrees of freedom available far below $T_N$ and the spin system is progressively searching for its true ground state. We believe the "bump" is correlated with the constantly increasing susceptibility below $T_N$ (see figures 4 - 6).

Our observations are in agreement with different magnetic structures found via neutron diffraction by Muñoz et al. [8], via Raman-scattering and infrared-active spectra studied by Iliev et al. [17] and via non-linear optical spectroscopy by Fröhlich et al. [18,19]. Thermal expansion measurements on single crystals are in progress for these hexagonal frustrated systems in order to give us a better picture of this "hidden" processes that occur at lower
temperatures.

V. DIELECTRIC SUSCEPTIBILITY

In general, one expects a coupling between ferroelectricity and magnetism only when $T_{FE}$ is close to $T_N$. However, a coupling between the ferroelectric and antiferromagnetic order parameters in YMnO$_3$ has been recently claimed by Huang et al. [12] based on the observation of a small "S"-shaped anomaly ($\sim2\%$) at the Neel temperature in the $\epsilon$ versus $T$ curve. They have suggested that such a coupling could arise due to the magnetostrictive effect associated with a lattice change accompanying the antiferromagnetic ordering of Mn$^{3+}$ spins. We also have measured the dielectric response of our high purity samples and our data reveal a more enhanced "S"-shaped curve - see $\square$. Note that the dielectric susceptibility, $\epsilon(T)$ is probed at $T_N \ll T_{FE}$ and that the step at $T_N$ is rather small. These leads us to believe that we are observing a magnetic ordering effect on the mobility of the domain walls of the ferroelectric domains and not a direct coupling between the two order parameters.

VI. DISCUSSIONS

For samples containing small amounts of impurity phase (Mn$_3$O$_4$ with $T_C = 43$ K) strong anomalies occurs around 43 K. For example, sharp spikes with small entropy contents appear in the specific heat [8] and there are strong "upturns" and field dependence in susceptibilities. Our specially prepared samples (see [4]), whose data are shown in the previous figures, are completely free of such anomalies. Therefore, we believe our samples are without the troublesome ferromagnetic impurity phase and the claims of unusual behavior around 40 K by other authors are the result of impure samples.

There is remarkable difference in the bulk properties of YMnO$_3$ and LuMnO$_3$ on one hand and those of ScMnO$_3$ at the other. The magnetic susceptibility of the former two compounds shows the characteristic kink at $T_N$, while the susceptibility of ScMnO$_3$ increases much more rapidly as temperature is decreased through the Neel point- see [8]. Also, the
magnetic susceptibility of ScMnO$_3$ is sensitive to magnetic history of the sample, i.e., there is a difference between the field cooled and zero-field cooled values even for magnetic fields as low as 50 mT. Such field dependent history is not found in low field $\chi$ measurement for the YMnO$_3$ nor for LuMnO$_3$.

Considering the specific heat at the lowest temperatures, one sees that the total specific heat of ScMnO$_3$ is proportional to $T^2$ up to a temperature of 30 K, while those of YMnO$_3$ and LuMnO$_3$ show a much stronger $T$ dependence (see inset of logarithmic scale). We would expect that the low temperature specific heat of an antiferromagnetic material can be described by a $T^3$ term due to phonons and antiferromagnetic spin-waves (possibly with an exponential term due to a gap at zero wave-vector in the spin-wave spectrum). Now, a $T^2$ dependence at low temperatures (below 30 K) shows that the specific heat is dominated by magnetic effects rather then by phonon excitations. Such a magnetic contribution which deviates from the antiferromagnetic spin-wave type indicates a ferromagnetic origin where the specific heat due to spin waves should follow $T^{3/2}$.

These subtle differences in the magnetic behavior are the subject of our neutron diffraction and muon spin rotation experiments on polycrystalline and single crystal materials of these fascinating Mn-oxides.

**VII. CONCLUSIONS**

We have synthesized for the first time polycrystalline samples of the hexagonal REMnO$_3$ compounds with a sufficient purity such that the antiferromagnetic magnetic ordering is revealed in the magnetic susceptibility. We have measured the specific heat and we show that an adequate analysis leads to the full entropy of the magnetic Mn-ions. We find that a considerable part of this entropy is released only at temperatures of order of half of the Neel temperature. There appears to be a remarkable difference between the properties of YMnO$_3$ and LuMnO$_3$ on the one hand and those of ScMnO$_3$ on the other. Finally, we have measured the dielectric susceptibilities, which shows a kink at the respective magnetic
transition temperatures. We believe this to be due to an influence from the antiferromagnetic ordering on the mobility of the ferroelectric domain-walls.

The authors gratefully acknowledge R.W.A. Hendrikx, and T.J. Gortenmulder for their technical assistance in analyzing the samples, H.B. Brom and I.G. Romijn for the use of their dielectric susceptibility apparatus and R. Feyerherm for valuable discussions. This work was supported by the Dutch Foundation FOM.

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TABLE I. Effective Mn moments, Neel temperatures, paramagnetic Curie-Weiss temperatures and frustration parameters.

|       | $\mu_{_{\text{eff}}}/\mu_B$ | $T_N$(K) | $\theta_{_{\text{CW}}}$$(\text{K})$ | $|\theta_{_{\text{CW}}} |/T_N$ |
|-------|----------------------------|----------|---------------------------------|----------------------------|
| YMnO$_3$ | 4.91                     | 71       | -417                            | 5.9                        |
| LuMnO$_3$ | 4.78                     | 90       | -519                            | 5.8                        |
| ScMnO$_3$ | 4.11                     | 130      | -495                            | 3.8                        |
FIG. 1. Low temperature susceptibility of YMnO$_3$ in a field of 2 T. The kink represents the Neel temperature. Inset: inverse susceptibility and the high-T Curie-Weiss fit (solid line).

FIG. 2. Low temperature susceptibility of LuMnO$_3$ in a field of 2 T. The kink represents the Neel temperature. Inset: inverse susceptibility and the high-T Curie-Weiss fit (solid line).

FIG. 3. Low temperature susceptibility of ScMnO$_3$ in a field of 2 T. The kink represents the Neel temperature. Inset: inverse susceptibility and the high-T Curie-Weiss fit (solid line).

FIG. 4. Excess specific heat (left scale) of YMnO$_3$ after subtraction of phonon contribution (see inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). $T_N$ is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

FIG. 5. Excess specific heat (left scale) of LuMnO$_3$ after subtraction of phonon contribution (see inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). $T_N$ is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

FIG. 6. Excess specific heat (left scale) of ScMnO$_3$ after subtraction of phonon contribution (see inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). $T_N$ is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

FIG. 7. Dielectric constant $\epsilon$ around the magnetic phase transition. The arrows represent $T_N$ determined from the $\chi$ and $\Delta C_p$ measurements.

FIG. 8. ZFC-FC susceptibility of ScMnO$_3$ in 0.05 T and 2 T. Inset: low temperature specific heat of YMnO$_3$, LuMnO$_3$ and ScMnO$_3$ on logarithmic scales.
\[ \chi \times 10^3 \text{(emu/mol)} \]

\[ T_N = 70 \text{K} \]
$\chi (\text{mole/emu})$

$T (\text{K})$

$T_N = 90 \text{K}$
$T_N = 130K$
\[ \frac{\Delta C_p}{T} = \frac{\Delta S}{T} \]

\[ \Delta C_p (J/mol \times K) \]

\[ \Delta S (J/mol \times K) \]

Graph showing the relationship between temperature (T in K) and the change in specific heat capacity (\( \Delta C_p \)) and entropy (\( \Delta S \)) for two different magnetic fields: 0T and 9T. The graphs indicate a peak near 100K for both fields, with the 9T field showing a more pronounced peak compared to the 0T field.
YMnO$_3$  
LuMnO$_3$  
ScMnO$_3$
