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The magnetic susceptibility, specific heat and dielectric constant of hexagonal $YMnO_3$, $LuMnO_3$ and $ScMnO_3$

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Abstract

We report the magnetic susceptibility, specific heat and dielectric constant for 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.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

1. Introduction

Rare-earth manganites of the perovskite-type structure $REMnO_3$ were discovered in the 1950s. Materials with small ionic radius (RE = Ho, Er, Tm, Yb, Lu, Y and Sc) crystallize in the hexagonal structure (space group: $P6_3cm$) while the compounds with larger ionic radius (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy) are orthorhombic (space group: $Pnma$) [1]. The orthorhombic compounds (space group: $Pnma$) form the basis for the colossal-magnetoresistance materials and they have been studied widely in recent years. Unlike the case for their orthorhombic counterparts, investigations on 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 the Mn^{3+} spins. Such magnetic ordering occurs in both structures; however, ferroelectricity is possible only for the hexagonal phase which has the non-centrosymmetric phase group $P6_3cm$. Although hexagonal manganates 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 up the possibility for electric–magnetic interactions and 'tuning' with electric and magnetic fields.

Current efforts are focused on the magnetic transition and refining the magnetic structure [7, 8, 10]. These investigations have been complicated by the formation of a ferromagnetic impurity phase, Mn_3O_4, with a Curie temperature $T_C \simeq 43$ K. Amounts of the order of 0.5 at.% of this phase are found in most samples reported on to date [2, 8, 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 than 0.1 at.%) of $YMnO_3$, $LuMnO_3$ and $ScMnO_3$. We have measured the magnetic susceptibility (χ) up to 400 K in different external fields. The specific heat (C_p) and its field dependence were also determined. Using a two-Debye-temperature model we can deduce the excess ΔC_p and the magnetic entropy. Finally, we have measured the dielectric constant (ϵ). 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.

2. 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 calcined in an O_2 flow at 1100 °C for 24 h. To ensure better homogeneity the mixtures were ground again, compacted into small pellets and reheated in air at 1400 °C for 48 h for $YMnO_3$ and $LuMnO_3$; and at 900 °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 reference [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 (δ) lack/excess in the oxygen stoichiometry, which may be such as $REMnO_{3\pm\delta}$. 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, 4, 6]. The radius of the pellets is 1.5 mm and their thickness varies from 0.5 mm to 0.8 mm.

The dc susceptibility (χ) 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 commonest impurity (Mn_3O_4) this leads to an

estimate of less than 0.05% of this impurity. We also estimated the amount of second phase in all samples by measuring the magnetization in different fields, which leads to even lower amounts. Finally we measured the dielectric constant ϵ as a function of the temperature using a capacitance bridge operating at a frequency of 1 MHz.

3. Susceptibility

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

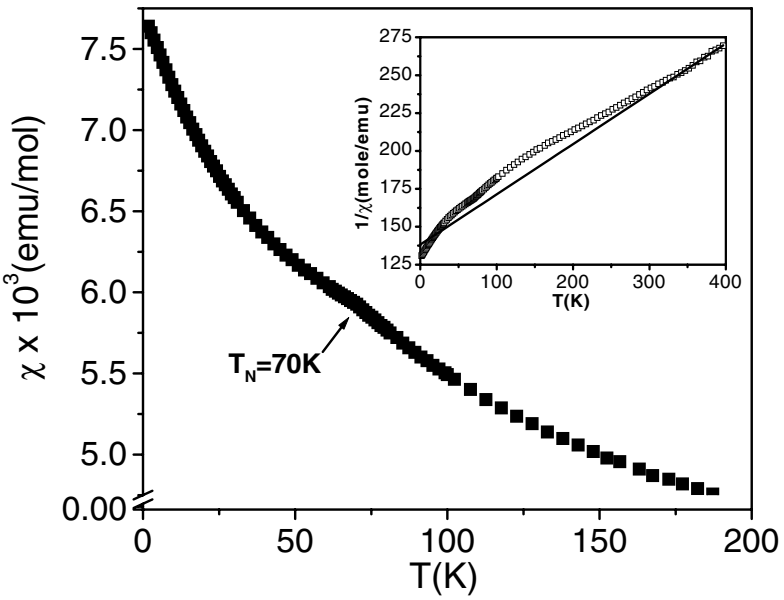

Figure 1. The low-temperature susceptibility of $YMnO_3$ in a field of 2 T. The kink represents the Néel temperature. Inset: the inverse susceptibility and the high-T Curie–Weiss fit (solid line).

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 findings combined with group theory arguments for this hexagonal lattice, Bertaut and Mercier [15] concluded that the Mn magnetic moments are directed in the basal plane and are oriented at angles of 120° with respect to each other. If the field is perpendicular to the magnetic plane all spins will be canted out of the plane by a small angle δ 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 at 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 on this intriguing behaviour.

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 (μ_{eff}) and the paramagnetic Curie temperatures (θ_{CW}) could be obtained. Table 1 collects these parameters together with T_N, taken as the temperature where the kink in χ versus T occurs.

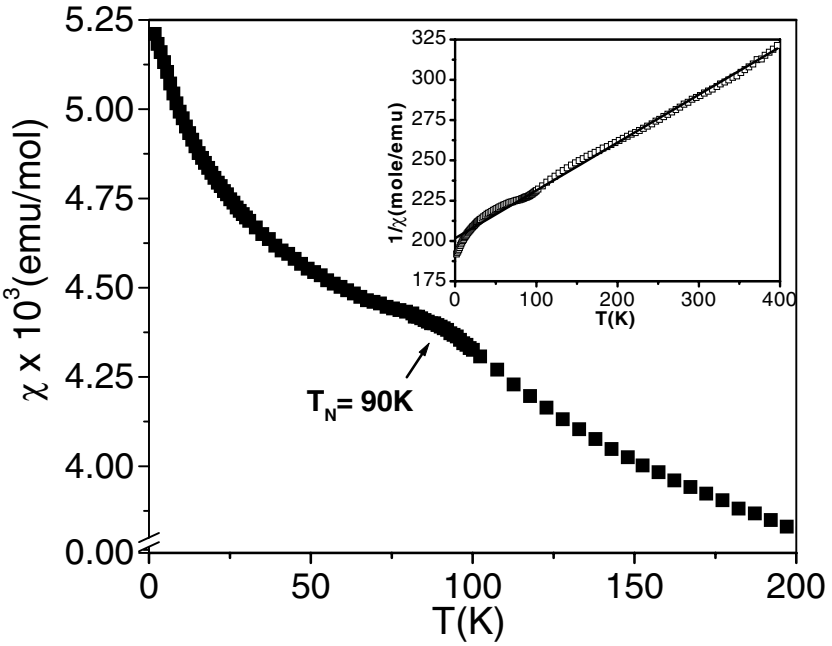

Figure 2. The low-temperature susceptibility of $LuMnO_3$ in a field of 2 T. The kink represents the Néel temperature. Inset: the inverse susceptibility and the high-T Curie–Weiss fit (solid line).

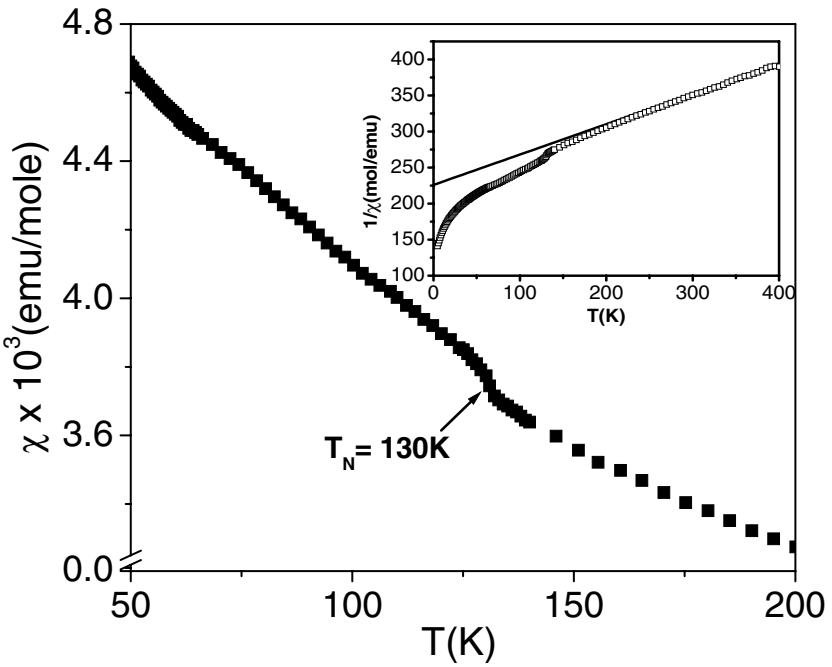

Figure 3. The low-temperature susceptibility of $ScMnO_3$ in a field of 2 T. The kink represents the Néel temperature. Inset: the inverse susceptibility and the high-T Curie–Weiss fit (solid line).

Table 1. Effective Mn moments, Néel temperatures, paramagnetic Curie–Weiss temperatures and frustration parameters.

	μ_{eff}/μ_B	T_N (K)	θ_{CW} (K)	$\lvert\theta_{CW}\rvert/T_N$
$YMnO_3$	4.91	71	−417	5.9
$LuMnO_3$	4.78	90	−519	5.8
$ScMnO_3$	4.11	130	−495	3.8

Because of the large values of θ_{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+} moment ($4.9\mu_B$). Also the absolute values of θ_{CW} are much larger than the ordering temperature T_N. Ramirez [16] defined the ratio between these parameters as a measure of the geometrical frustration of the antiferromagnetic system. For our in-plane triangular lattice this 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_3O_4) content of less than 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_3O_4, meaning that its abundance is less than 100 ppm.

4. 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 figure 4, figure 5 and figure 6 together with the estimates for

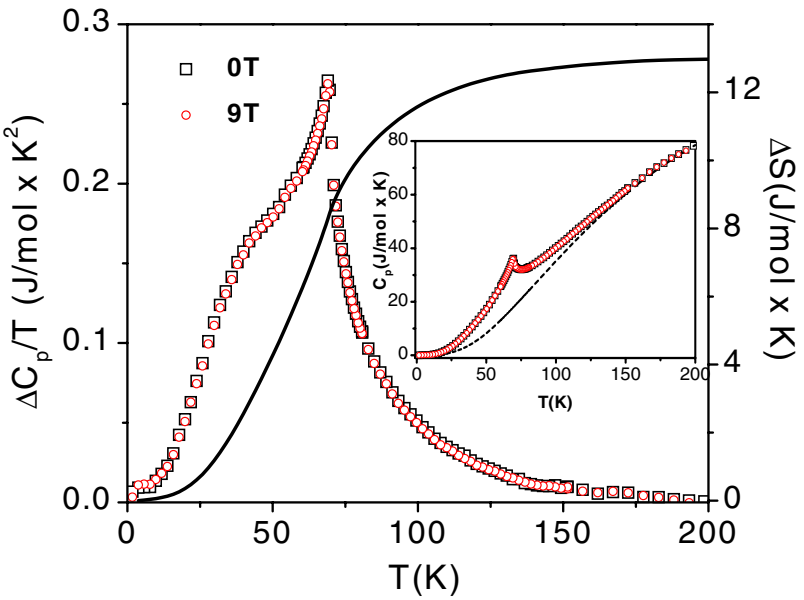

Figure 4. The excess specific heat (left scale) of $YMnO_3$ after subtraction of the phonon contribution (see the inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). T_N is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

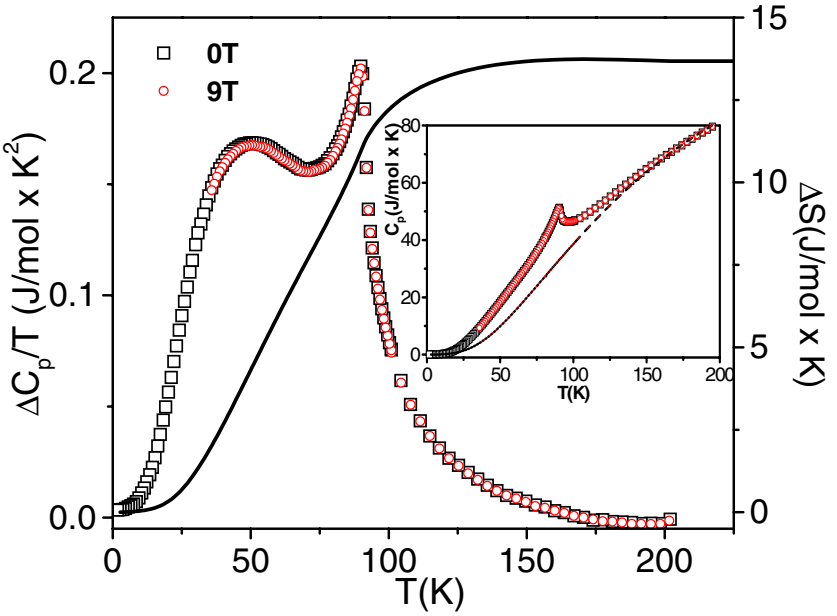

Figure 5. The excess specific heat (left scale) of $LuMnO_3$ after subtraction of the phonon contribution (see the inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). T_N is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

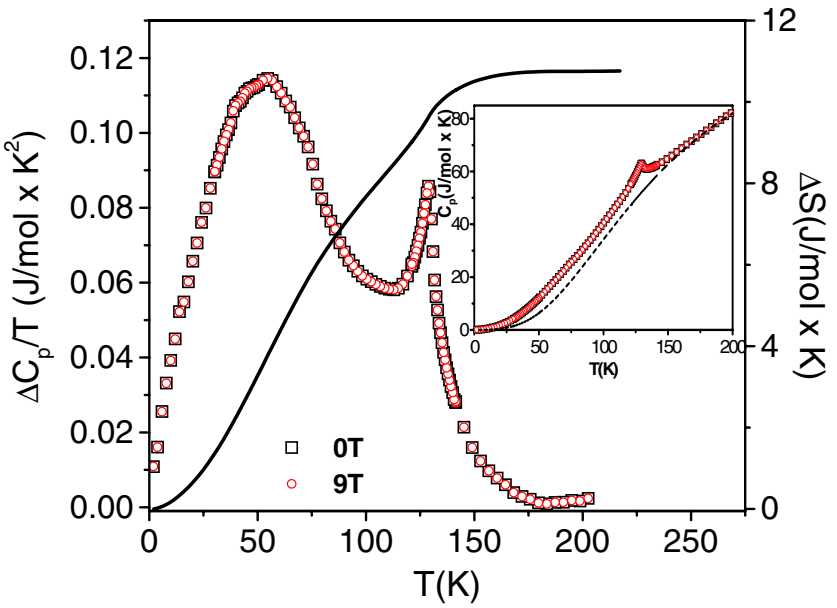

Figure 6. The excess specific heat (left scale) of $ScMnO_3$ after subtraction of the phonon contribution (see the inset). There is no change in a field of 9 T. The solid line represents the entropy (right scale). T_N is given by the peak in $C_p(T)$. The dashed line in the inset shows the lattice contribution.

their lattice contributions (dashed 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., θ_D('light') $\approx$ 780 K–800 K and θ_D('heavy') $\approx$ 350 K–420 K. Subtraction of this estimate of the lattice specific heat provides us with the (excess) magnetic contribution of the system. These ΔC_p are shown as $\Delta C_p/T$ versus T curves in figure 4, figure 5 and figure 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. Unlike previous workers [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 (Mn_3O_4). The resulting entropy is in excellent agreement with that expected for a Mn^{3+} ion ($S = 2$):

$$\Delta S = R \ln(2S + 1) = 13.38 \text{ J mol}^{-1} \text{ K}^{-1}.$$

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 ΔS of at least 90% of the expected one. Note that the magnitude of ΔC_p at T_N is approximately the same for all three compounds (18 J mol^{-1} K^{-1}).

Furthermore, there is an the 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 that 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 these 'hidden' processes that occur at lower temperatures.

5. 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 ($\sim$2%) at the Néel temperature in the ϵ 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 figure 7. 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. This 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.

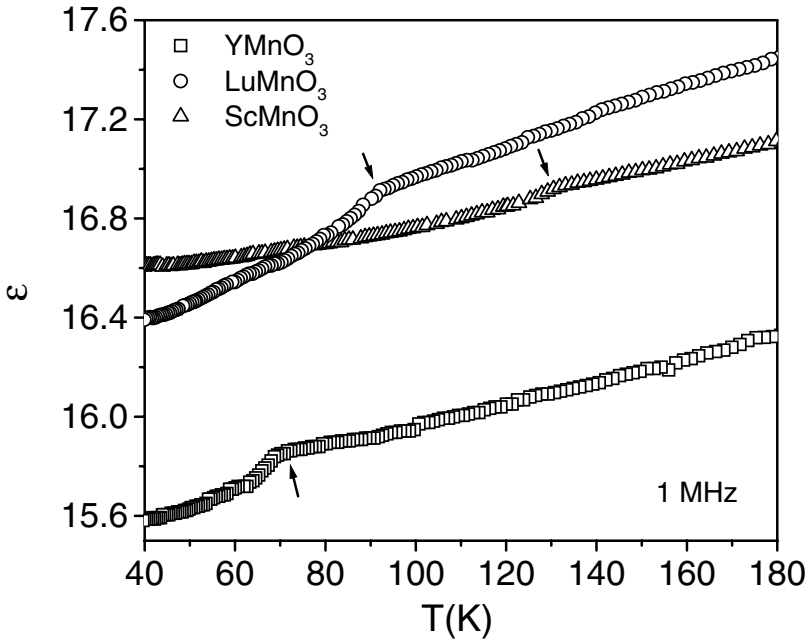

Figure 7. The dielectric constant ϵ around the magnetic phase transition. The arrows represent T_N determined from the measurements of χ and ΔC_p.

6. Discussion

For samples containing small amounts of impurity phase (Mn_3O_4 with $T_C = 43$ K), strong anomalies occur around 43 K. For example, sharp spikes with small entropy contents appear in the specific heat [8] and there are strong 'upturns' and field dependences of the susceptibilities. Our specially prepared samples (see section 2), whose data are shown in the previous figures, are completely free of such anomalies. Therefore, we believe that our samples are free of the troublesome ferromagnetic impurity phase and that the claims of unusual behaviour around 40 K made by other authors are the result of impure samples.

There is remarkable difference between the bulk properties of $YMnO_3$ and $LuMnO_3$ on one hand and those of $ScMnO_3$ on 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 Néel point—see figure 8. Also, the magnetic susceptibility of $ScMnO_3$ is sensitive to the 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 the low-field χ measurement for $YMnO_3$ 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 the inset of figure 8—logarithmic scale). We would expect the low-temperature specific heat of an antiferromagnetic material to be describable 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 than by phonon excitations. Such a magnetic contribution which

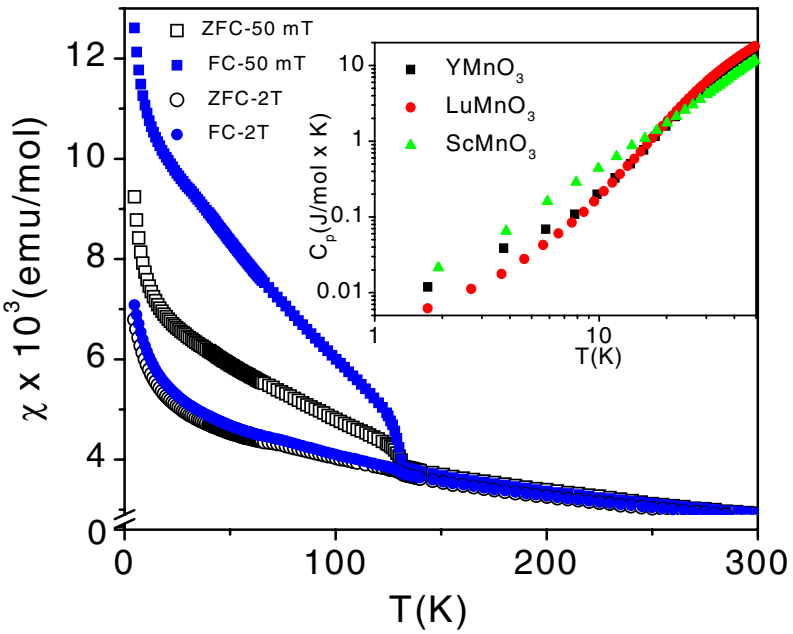

Figure 8. The ZFC–FC susceptibility of $ScMnO_3$ in 0.05 T and 2 T. Inset: the low-temperature specific heat of $YMnO_3$, $LuMnO_3$ and $ScMnO_3$ on logarithmic scales.

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 behaviour are the subject of our neutron diffraction and muon spin-rotation experiments on polycrystalline and single-crystal samples of these fascinating Mn oxides.

7. Conclusions

We have synthesized for the first time polycrystalline samples of the hexagonal $REMnO_3$ compounds with a sufficient purity 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 the order of half of the Néel 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 show kinks 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.

Acknowledgments

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