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LETTER TO THE EDITOR

Colossal magnetoresistance in $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$
($x = 0.0, 0.1$)

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Abstract. Magnetization and magnetotransport measurements have been used to study the composition dependence of the electronic properties of the Ruddlesden–Popper phases $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$. Although their behaviour differs in detail, both compounds show a colossal magnetoresistance (CMR) effect ($>10\,000\%$ in 14 T) in the temperature range $4.2 \leq T/\text{K} \leq 100$. However, neither material shows a transition to a ferromagnetic state above 4.2 K, and both materials have higher resistivities ($>10^3 \Omega \text{ cm}$ for $4.2 \leq T/\text{K} \leq 100$) than the metallic oxides previously found to show CMR. In view of the low conductivity and the absence of ferromagnetism, the CMR of these phases is not readily explained by a double-exchange mechanism.

The observation of colossal magnetoresistance (CMR) at the Curie temperature (T_C) of $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ perovskites has attracted considerable attention [1, 2, 3, 4], and a similar behaviour has recently been observed in the pyrochlore $\text{Tl}_2\text{Mn}_2\text{O}_7$ [5]. The effect is greatest close to T_C in these metallic oxides because the application of a magnetic field is thought to reduce the spin-disorder scattering of the conduction electrons in this region. Here we describe new CMR materials, structurally related to the perovskites yet with quite different physical properties, in which extensive chemical control can be exercised over the magnetotransport. CMR in these new non-metallic, layered compounds is not associated with complete ferromagnetic order or zero-field metal–insulator transitions, thus placing new constraints on the development of microscopic models for the effect.

The inclusion of different crystal structures in the search for an optimized CMR material is clearly important. Our research has focused on the $n = 2$ member of the series of Ruddlesden–Popper (RP) phases [6] $\text{A}_{n+1}\text{Mn}_n\text{O}_{3n+1}$ (figure 1), where n can be thought of as the number of layers of vertex-sharing MnO_6 octahedra which form structural blocks along the c -axis of the unit cell. The perovskite structure corresponds to the $n = \infty$ member of this series, and $n = 1$ is the well-known K_2NiF_4 structure. The structural consequences of moving from perovskite to $n = 2$ RP phases are the introduction of a two-dimensional character and a concomitant reduction from six to five in the number of nearest-neighbour Mn cations around a particular transition metal site. The reduction in the number of nearest neighbours is expected to produce an anisotropic reduction in the width of the energy bands derived (largely) from the Mn 3d orbitals, and hence to modify the electrical conductivity

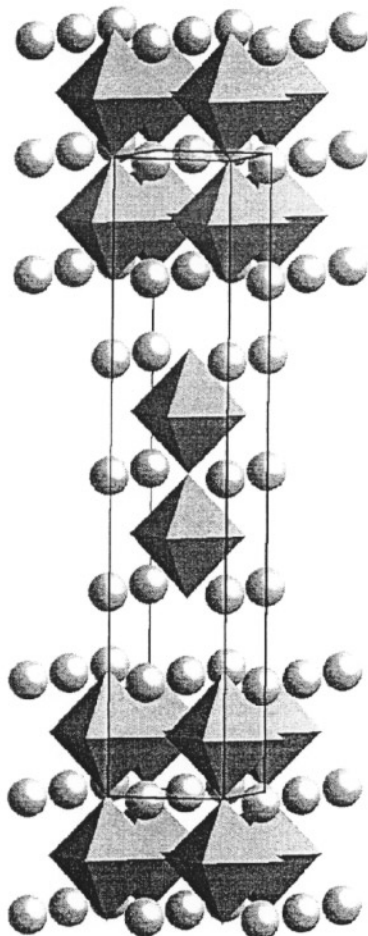


Figure 1. The crystal structure of $\text{Sr}_2\text{NdMn}_2\text{O}_7$; MnO_6 octahedra are shaded, Sr/Nd atoms are drawn as spheres.

and magnetic behaviour of these materials. We have recently observed that the onset of weak ferromagnetism in $\text{Sr}_2\text{LaMn}_2\text{O}_7$ is accompanied by a change in sign of $d\rho/dT$ [7], indicating that the strong coupling between electrical and magnetic properties seen in the perovskites carries over into the RP phases. However, no phase transitions were observed in the Curie–Weiss paramagnet $\text{Sr}_2\text{TbMn}_2\text{O}_7$ over the temperature range $5 \leq T/\text{K} \leq 290$, thus demonstrating that the properties of these systems are subject to chemical control. Morimoto *et al* [8] have recently shown that the composition $\text{Sr}_{1.8}\text{La}_{1.2}\text{Mn}_2\text{O}_7$ shows CMR around a Curie temperature of 126 K, the link between the CMR and ferromagnetism being reminiscent of both the perovskites and the pyrochlore. We have now extended our studies to include $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$, and the striking results of our magnetoresistance and magnetization measurements are described below.

Polycrystalline samples of $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ ($x = 0.0, 0.1$) were prepared by firing stoichiometric quantities of dry Nd_2O_3 , MnO_2 and SrCO_3 in alumina boats in air at 1300°C for five days after pre-firing at lower temperatures ($800, 1000$ and 1200°C

for one day each). X-ray powder diffraction data were collected on the final products using a Siemens D5000 diffractometer operating with Cu $K\alpha$ radiation in Bragg–Brentano geometry. Compositions were confirmed by ICP atomic emission analysis: the observed (and calculated) percentages are (i) $\text{Sr}_2\text{NdMn}_2\text{O}_7$: Sr 32.68 (32.37), Nd 26.88 (26.63), Mn 20.47 (20.30); (ii) $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$: Sr 30.29 (30.43), Nd 29.12 (29.00), Mn 20.31 (20.01). Magnetization measurements were performed on a Quantum Design MPMS magnetometer in the temperature range $4.2 \leq T/\text{K} \leq 290$ in magnetic fields of between 0 and 5 T. Where appropriate, measurements were taken after both zero-field cooling (ZFC) and cooling in the measuring field (FC). The preparation and magnetic properties of $\text{Sr}_2\text{LaMn}_2\text{O}_7$ have been described previously [7]. Magnetotransport measurements were carried out on all of the samples in magnetic fields of up to 14 T using a standard four-terminal method.

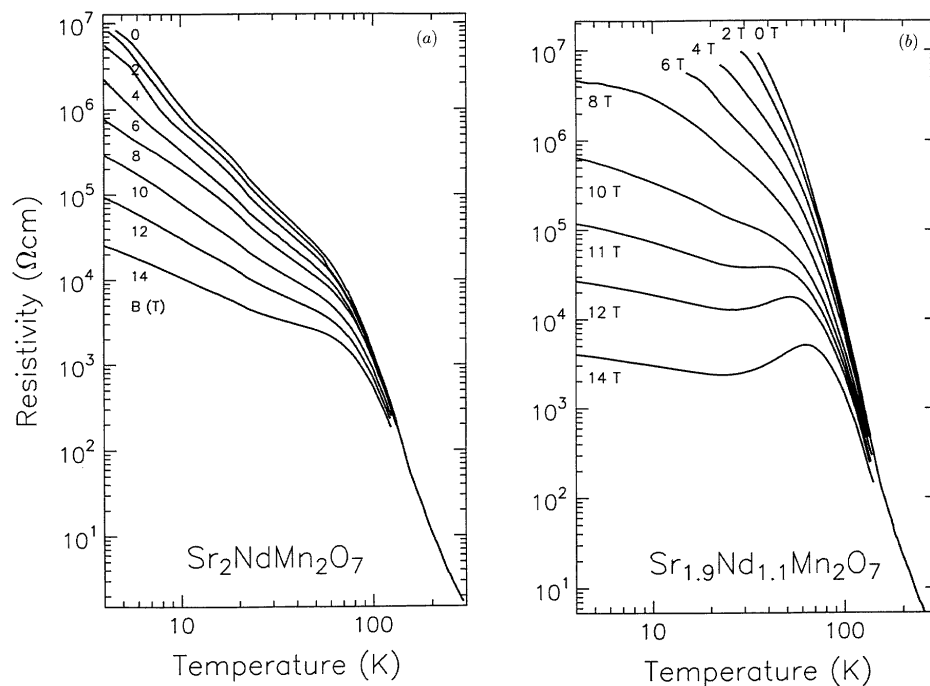


Figure 2. Resistivity as a function of temperature and applied field for (a) $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and (b) $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$.

The x-ray diffraction patterns of $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ could be indexed in the tetragonal space group $I4/mmm$ with $a = 3.8493(1)$, $c = 19.9650(6)$ Å ($x = 0.0$) and $a = 3.8449(1)$, $c = 20.0542(7)$ Å ($x = 0.1$) and were thus consistent with the adoption of an $n = 2$ RP structure. The resistivities of these two samples are shown as a function of magnetic field and temperature in figure 2. The measurements were made on polycrystalline sinters and the absolute values of the resistivity must therefore be treated with caution. However, a number of clear trends emerge. Both the increased magnitude and the much more pronounced temperature dependence of the resistivities compared with those of $\text{Sr}_2\text{LaMn}_2\text{O}_7$ (note the log scale on figure 2 and the linear scale on figure 3) suggest that the $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ samples are non-metallic. The zero-field resistivity of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ increases rapidly with decreasing temperature and changes gradient markedly below 100 K. Between room temperature and 100 K the fitted activation energies are

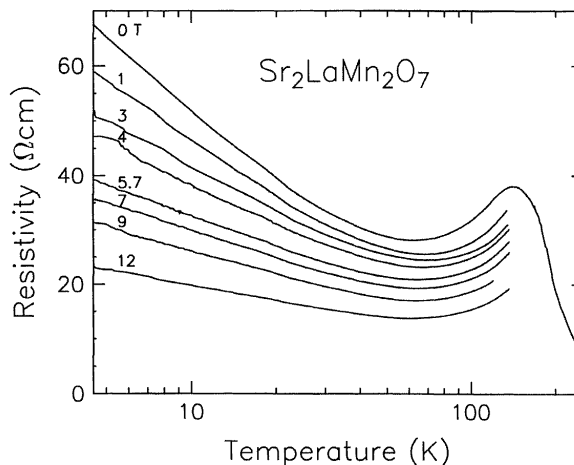


Figure 3. Resistivity as a function of temperature and applied field for $\text{Sr}_2\text{LaMn}_2\text{O}_7$.

0.091 eV and 0.109 eV for $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$ respectively. Application of a magnetic field produces a dramatic reduction in resistivity which is most pronounced below 100 K.

The magnetoresistance ratio $(\rho_B - \rho_0)/\rho_B$ is $-40\,000\%$ for $\text{Sr}_2\text{Nd}_2\text{Mn}_2\text{O}_7$ at 4.2 K and 14 T, although it is important to note that the resistivity still remains large (compared with $10^{-2} \Omega \text{ cm}$ for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x \sim 0.3$ [4]) and activated, rather than metallic, in the CMR regime. The zero-field resistivity of $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$, with a higher formal Mn^{3+} concentration, is higher than that of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and increases more markedly with decreasing temperature, without changing slope (at ~ 100 K). The resistivity decreases very sharply when a magnetic field is applied (magnetoresistance ratio of $-300\,000\%$ at 40 K in a 14 T field—the zero-field resistivity becomes unmeasurably large below this temperature), and a maximum in the resistivity develops in fields above 10 T ($T_{max} = 50$ K, 11 T; 70 K, 14 T). The comparison of the Nd phases with $\text{Sr}_2\text{LaMn}_2\text{O}_7$ (figure 3) below the spin-canting temperature indicates that the more conducting $n = 2$ RP phases have smaller magnetoresistances; the MR ratio of $\text{Sr}_2\text{LaMn}_2\text{O}_7$ is only $\sim 200\%$ at 4.2 K and 12 T.

The magnetization data for these compounds are not readily interpreted using simple models. The molar magnetic susceptibility of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ is drawn as a function of temperature and field in figure 4. The FC data show a marked field dependence over the entire temperature range, and the same behaviour is apparent over a wide temperature range in the ZFC data. The most obvious features in the data are a susceptibility maximum at 210 K, the onset of hysteresis below 135 K, and a local maximum at 26 K. The molar magnetic susceptibility of $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$ is plotted as a function of temperature in figure 5. The temperature variation is markedly different from that of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ and measurements in fields of 0.01 and 5.0 T showed that the magnetization is strongly field dependent. The most striking feature of the data on both compositions is that in neither case is there evidence for ferromagnetism at any temperature.

The data presented above show a wide variation in the physical properties of three isostructural compounds which have very similar chemical compositions. The sensitivity of the magnetoresistance of these $n = 2$ RP phases to the atomic number and to the concentration of the lanthanide element is even greater than has been seen in the $n = \infty$

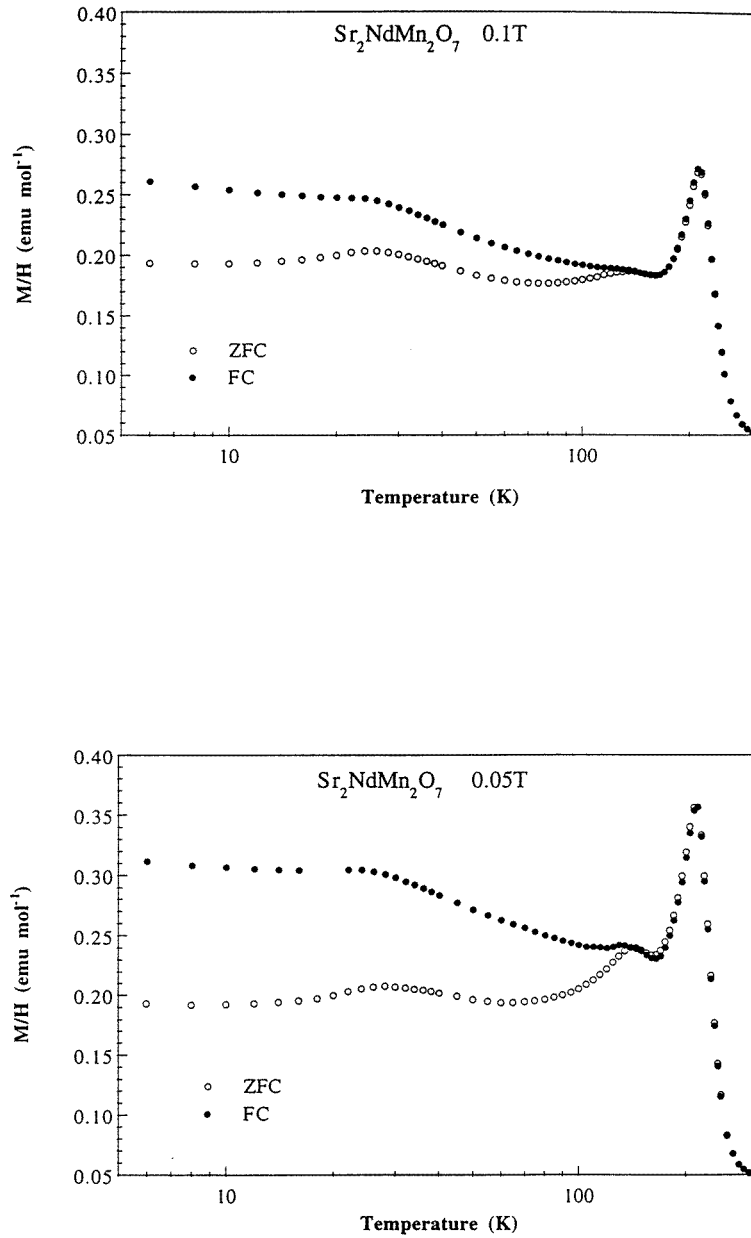


Figure 4. The molar magnetic susceptibility of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ as a function of the temperature and measuring field.

perovskites, thus suggesting that there is more scope for tuning the properties of the low-dimensional system by chemical control of both the carrier concentration and the interatomic distances, and hence bandwidths. $\text{Sr}_2\text{LaMn}_2\text{O}_7$ is the only one of the compounds to be discussed which shows clear evidence for a spontaneous magnetization, albeit only $0.35 \mu_B$ per Mn site, at low temperatures (<130 K [7]), and also the only one to show

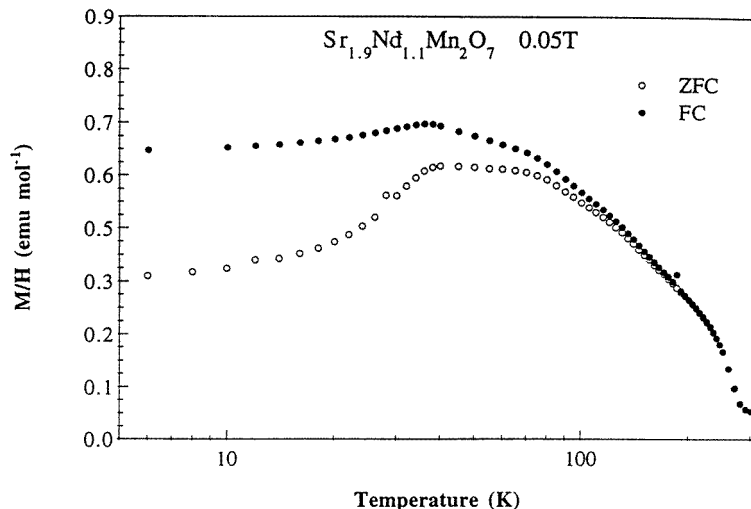


Figure 5. The molar magnetic susceptibility of $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$ as a function of temperature in a field of 0.05 T.

a resistivity maximum in the absence of a magnetic field. Our neutron diffraction data [9], which will be described in full in a subsequent publication, show that the low-temperature phase is predominantly antiferromagnetic ($T_N = 210$ K), and the magnetization is therefore probably due to a weak spin-canting. This sample is set apart from the perovskites and $\text{Sr}_{1.8}\text{La}_{1.2}\text{Mn}_2\text{O}_7$ [8] by the observation of significant, though not colossal, magnetoresistance in a metallic phase which is not truly ferromagnetic†. It is also set apart from the insulating K_2NiF_4 phase $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4$ which, although it too contains Mn in an average oxidation state of 3.5, is a spin glass [10] which shows no evidence of long-range magnetic order at 2 K [11]. It thus appears that the properties needed for the observation of magnetoresistance effects can be preserved in the RP system for $2 \leq n \leq \infty$, but that they may not carry over into the more two-dimensional $n = 1$ phase.

The behaviour of $\text{Sr}_2\text{NdMn}_2\text{O}_7$ is more remarkable than that of the La analogue in that CMR is observed over a wide temperature range in a material with a resistivity six orders of magnitude greater than that typical of a metallic oxide. The magnetic susceptibility of this compound shows a complex temperature dependence, but there is no evidence for the onset of even weak ferromagnetism at any point. The susceptibility maximum at 210 K is not due to long-range magnetic ordering of the spins on the Mn sublattice [9], and we tentatively suggest the formation of superparamagnetic clusters [12] at this temperature. This would be consistent with the observed field dependence of the non-hysteretic susceptibility. The local maximum at ~ 140 K is associated with the onset of long-range antiferromagnetic order on the Mn sublattice [9], but the difference between the ZFC and FC data below this temperature suggests that some frozen-in magnetic disorder is also present. The absence of an increase in the susceptibility on cooling leads us to suggest that the Nd^{3+} magnetic moments are frozen but disordered in this temperature region. We then ascribe the local maximum at 26 K to the long-range magnetic ordering of the Nd^{3+} cations.

The magnetization of $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$ (nominal oxidation state of Mn: 3.45+),

† *Note added in proof.* It now seems possible that our sample of $\text{Sr}_2\text{LaMn}_2\text{O}_7$ has two components: a majority, antiferromagnetic phase, and a minority, ferromagnetic phase similar to that reported by Morimoto *et al* [8].

recorded in a field of 0.05 T, also shows magnetic frustration, but no spontaneous magnetization, at low temperatures. However, both the susceptibility and the magnetotransport data are very different from those collected on $\text{Sr}_2\text{NdMn}_2\text{O}_7$ (nominal oxidation state of Mn: 3.50+), once again emphasizing the importance of chemical composition in these systems. Long-range magnetic ordering is suppressed in $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$, and only occurs below ~ 100 K [9]. The increase in the susceptibility at ~ 210 K, which we ascribed above to the formation of superparamagnetic clusters, is much less marked in $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$. However, the magnitude of the negative magnetoresistance parameter is much greater in $\text{Sr}_{1.9}\text{Nd}_{1.1}\text{Mn}_2\text{O}_7$, and a maximum is evident in the temperature dependence of the resistivity measured in fields of greater than 10 T. In neither compound is there a direct correspondence between the temperatures of the magnetic phase transitions and the temperatures associated with changes in the magnetotransport behaviour, although both occur in the region of 100 K and the measuring fields were significantly different. We are currently preparing a wide range of compositions in the $n = 2$ RP system to establish how large an effect we can engineer chemically. The high sensitivity of properties to stoichiometry requires very careful control of synthesis conditions in this work.

The effects seen in $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ clearly require theoretical explanation. Previous discussions on the perovskite systems have focused on charge ordering of Mn^{3+} and Mn^{4+} , and on the possible involvement of magnetic polarons. These may be important in some or all of the $n = 2$ RP phases, but the fact that our materials are antiferromagnetic insulators which show CMR over a wide temperature range, rather than ferromagnetic metals which show the effect close to T_C , makes us wary of relying too heavily on the models used to describe perovskites. The absence of a metamagnetic transition in fields of up to 5 T together with the smooth temperature dependence of the resistivity in fields of up to 14 T suggest that an explanation based upon the melting of a charge-ordered state [13] is unlikely. Furthermore, it is not clear that we can rely on the double-exchange mechanism to account for our results on antiferromagnetic $\text{Sr}_{2-x}\text{Nd}_{1+x}\text{Mn}_2\text{O}_7$ unless the CMR is strongly linked to that part of the structure which is a magnetic glass and may therefore be more susceptible to spin reorientation by an applied field. The validity of the double-exchange model has recently been questioned even in the case of the perovskites [14], and it has been argued that Jahn–Teller coupling is a key factor [15, 16]. If this is the case, the tetragonal symmetry inherent in the Ruddlesden–Popper structure may be important in explaining the differences between the phases reported here and the perovskites. We are further exploring the magnetic properties of these materials using muon-spin rotation experiments.

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