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LETTER TO THE EDITOR

Physical properties of the $n = 3$ Ruddlesden–Popper compound $Ca_4Mn_3O_{10}$

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Abstract. We present the results of a combined magnetization, muon-spin rotation, transport and magnetotransport study of the $n = 3$ Ruddlesden–Popper (RP) compound $Ca_4Mn_3O_{10}$. This compound adopts a layered structure in which groups of three perovskite layers alternate with single rock-salt layers. The muon-spin rotation data show that there is a sharp magnetic phase transition at 115 K. The resistance and magnetoresistance of the sample show no particular features at this temperature, but the transition affects the energy barriers associated with hopping transport. The magnetoresistance is proportional to the square of the magnetization, and is largest at low temperatures; a 40% drop in resistivity is observed in a magnetic field of 14 T at 61 K, much smaller than that measured in the related $n = \infty$ RP (perovskite) manganites which exhibit colossal magnetoresistance (CMR).

The recent renewal of interest in the magnetotransport properties of metal oxides stems from the discovery [1, 2] of colossal magnetoresistance (CMR) in perovskites of the form $Ln_{1-x}A_xMnO_3$, where the presence of both the trivalent lanthanide (Ln) and the divalent (A) cations results in the adoption of a non-integral oxidation state (Mn^{3+}/Mn^{4+}) of the Mn cation [3]. The physics underlying the CMR effect in these materials is thought to be associated with double exchange [4], although it appears that other mechanisms may play a role [5].

This class of perovskite materials can be regarded as the $n = \infty$ member of a general family of compounds $(Ln,A)_{n+1}Mn_nO_{3n+1}$, known as Ruddlesden–Popper (RP) phases [6]. The $n = 1$ member has the K_2NiF_4 structure and consists of single perovskite layers alternating with rock-salt layers. For general n the composition can be rewritten $[(Ln,A)MnO_3]_n[(Ln,A)O]$, illustrating the fact that RP phases consist of n layers of perovskite alternating with single rock-salt layers. Thus, by changing n, one can progressively decouple the perovskite layers and tune the effective dimensionality of the interactions from fully three-dimensional in the case of $n = \infty$, to two-dimensional in the case of $n = 1$. CMR has been observed [7, 8, 9] for $n = 2$, and it is has been shown that, as for the $n = \infty$ systems, the magnetotransport and magnetic properties depend crucially on the choice of lanthanide and the level of doping [10, 11, 12].

In this letter we present measurements of the physical properties of an $n = 3$ RP phase, $Ca_4Mn_3O_{10}$. The crystal structure of $Ca_4Mn_3O_{10}$ is shown in figure 1 and illustrates how

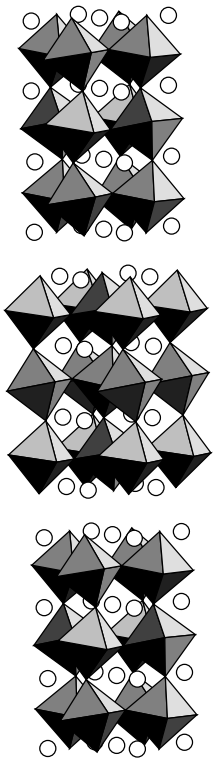

Figure 1. Crystal structure of $Ca_4Mn_3O_{10}$; MnO_6 octahedra are shaded and Ca atoms are shown as spheres.

groups of *three* perovskite layers alternate with rock-salt layers. $Ca_4Mn_3O_{10}$ is an oxide of Mn(IV) and therefore might not be expected to show interesting magnetotransport properties because of the absence of mixed valence. However, as demonstrated in experiments on the pyrochlore $Tl_2Mn_2O_7$, CMR can occur even in the absence of mixed valence [13, 14].

Polycrystalline samples of $Ca_4Mn_3O_{10}$ were prepared by reacting well-ground stochiometric mixtures of $CaCO_3$ and MnO_2. Details of the preparation are described elsewhere [15]. The purity of the products was established using x-ray powder diffraction data collected on a Siemens D5000 diffractometer operating with Cu Kα_1 radiation. It was found that the oxygen stoichiometry is not perfect, so that the formula is $Ca_4Mn_3O_{10-\delta}$; however δ is less than 0.04 [15].

The magnetic susceptibility was determined in the temperature range $5\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$ using a SQUID magnetometer. Data were collected after cooling the sample in the absence of an applied magnetic field (zero-field cooled, ZFC) and after cooling the sample in a measuring field of 0.05 T (field cooled, FC). The magnetization isotherms were measured up to a field of 5 T.

Muon-spin rotation/relaxation (μSR) measurements were carried out on the MuSR/EMU beamlines at ISIS (Rutherford Appleton Laboratory, UK), and also using the GPD spectrometer on the πM3 beamline at the Paul Scherrer Institute (PSI) in Switzerland. Spin-polarized positive muons were implanted in a sample of $Ca_4Mn_3O_{10}$ (mounted on a silver backing plate and cooled in a He^4 cryostat) and the depolarization of the muon spin was measured by monitoring the time-dependence of the angle-dependent decay positron emission (this occurs predominantly along the instantaneous direction of the muon spin). For the zero-field measurements the earth's magnetic field was compensated to less than

10 μT. The data are conventionally presented by comparing the positron counts in the forward and backward detectors and forming an asymmetry function $P(t)$, a quantity which is then proportional to the time-evolution of the muon spin polarization [16]. μSR has been used extensively to study subtle magnetic properties in a wide range of materials [17].

The temperature dependence of the molar magnetic susceptibility χ of the sample $Ca_4Mn_3O_{10}$ is shown in figure 2(a). The magnetic behaviour is complex. In the paramagnetic (high temperature) regime, χ^{-1} follows a Curie–Weiss-like behaviour with a negative intercept at $T = -500 \pm 50$ K and a gradient corresponding to 4.54 μ_B per Mn ion (figure 2(a), inset). The ZFC magnetization data are most characteristic of an *antiferromagnetic* state, existing below a well-defined transition at 115 K, in qualitative agreement with neutron-scattering studies [15]. The increase in magnetization at low temperatures (FC) suggests that the sample also acquires a small spontaneous magnetization (0.005 μ_B/Mn; figure 2(a)), as also shown by the presence of hysteresis in the magnetization isotherms of figure 2(b) [15].

The weak ferromagnetism [18] in the low-temperature phase ($T \leqslant 115$ K) is most probably due to the canting of predominantly antiferromagnetically arranged spins away from the *ab* plane and along the *c*-axis caused by the Dzyaloshinskii–Moriya interaction [19]. This could arise as a result of the slight tilting of the MnO_6 octahedra on the edges of perovskite blocks which is known to occur [15], removing the centre of inversion at the oxygen sites [20].

Further evidence of the complexity of the low-temperature phase comes from studies of the decay of the remanent magnetization at constant temperature [20]. At temperatures less than 115 K, the time dependence of the remanent magnetization is well described by a stretched exponential law, corresponding to a spin glass, rather than the power law typical of ferromagnetic order [21]. The spin–glass-like behaviour of the remanent magnetization is attributable to an inhomogeneous distribution of the canted moments, associated with the inhomogeneous distribution of structural distortions [15].

Muon-spin relaxation data taken using the ISIS facility are presented in figure 3. For temperatures above the transition a Gaussian-like relaxation is observed which corresponds to relaxation due to the nuclear spins (the electronic spins are fluctuating very fast in this regime and are therefore too fast to be observed due to a motional narrowing effect [22]). There is very little temperature dependence in the muon relaxation between 300 K and 115 K. Below 115 K the muons are depolarized extremely rapidly and no relaxation is observed. This implies an extremely sharp magnetic ordering transition. The sharpness of the transition is in stark contrast to the broad transitions which have been observed [23] in the $n = 2$ systems $Sr_2LnMn_2O_7$. In those systems the ordering process appears to be associated with formation of spin clusters. The sudden transition which we observe in $Ca_4Mn_3O_{10}$ appears to be a true phase transition to an ordered state, and not a progressive evolution of short-range ordered domains. In our experiments at ISIS no oscillations due to the muon precession in the ordered state of $Ca_4Mn_3O_{10}$ can be observed. The large magnitude of the internal field in the ordered state renders oscillations undetectable at a pulsed muon source such as ISIS. However experiments at PSI (a continuous source of muons which thus has an improved frequency resolution) failed to find evidence of a rotation signal in the ordered state, suggesting that the muons were depolarized in less than 10 ns.

Magnetoresistance measurements were carried out on a sintered bar using a four-terminal method with a direct current of less than 50 μA. The current–voltage dependence showed ohmic behaviour over the entire temperature range studied and the current was reversed during measurements to eliminate the effects of thermal voltages. The sample was mounted in a variable-temperature insert which was loaded into a 17 T superconducting magnet.

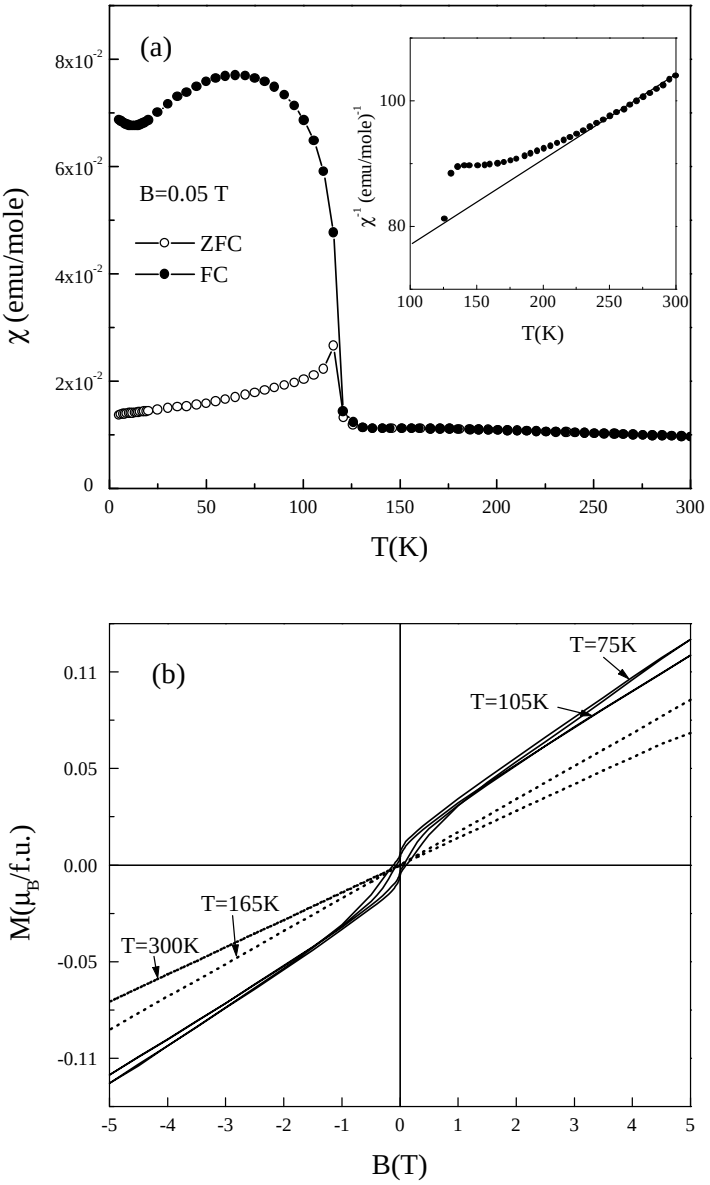

Figure 2. (a) Molar magnetic susceptibility χ of $Ca_4Mn_3O_{10}$ as a function of temperature, cooled in zero field (ZFC) (open circles), or in a field of 0.05 T (FC) (solid circles). The inset shows a Curie–Weiss fit (line) for $T \geqslant 240$ K to the data (points). (b) Magnetization in $Ca_4Mn_3O_{10}$ as a function of magnetic field for different temperatures above (dotted lines) and below (solid lines) the magnetic transition at 115 K.

The measured temperature dependence of the resistivity of $Ca_4Mn_3O_{10}$ in zero-field and at 14 T is shown in figure 4. The magnetoresistance is very small at high temperatures but becomes more significant at low temperatures (note the log scale on the resistivity axis). In contrast to the behaviour of magnetization, which shows a clear transition at 115 K, the resistivity increases strongly as the temperature decreases and does not show any strong

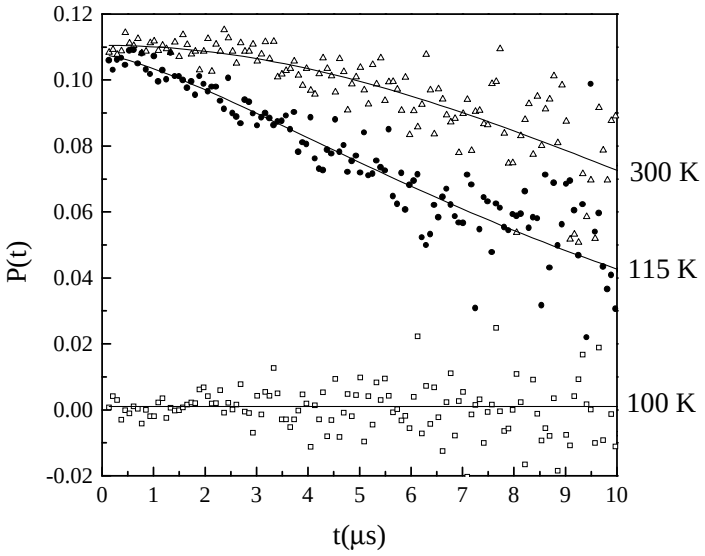

Figure 3. Muon-spin relaxation data for $Ca_4Mn_3O_{10}$ for three different temperatures. The decay positron asymmetry $P(t)$ has been corrected for a background relaxation resulting from the sample holder. The initial asymmetry at high temperatures corresponds to the full polarization of the muon beam.

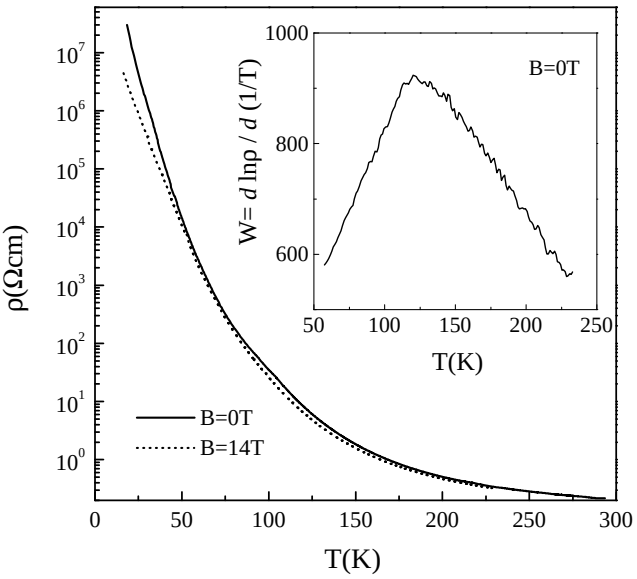

Figure 4. Electrical resistivity of $Ca_4Mn_3O_{10}$ as a function of temperature in zero-field and in a magnetic field of 14 T. The inset shows the effective activation energy $W = [\mathrm{d}\ln\rho/\mathrm{d}(1/T)]$ extracted from the zero-field resistivity.

feature in the raw data at 115 K. However, the effective activation energy (defined as $W = [\mathrm{d}\ln\rho/\mathrm{d}(1/T)]$) (see figure 4, inset) in zero field shows that the transport is affected by the magnetic transition; for $T > 115$ K, the slope of W versus T is negative, whereas

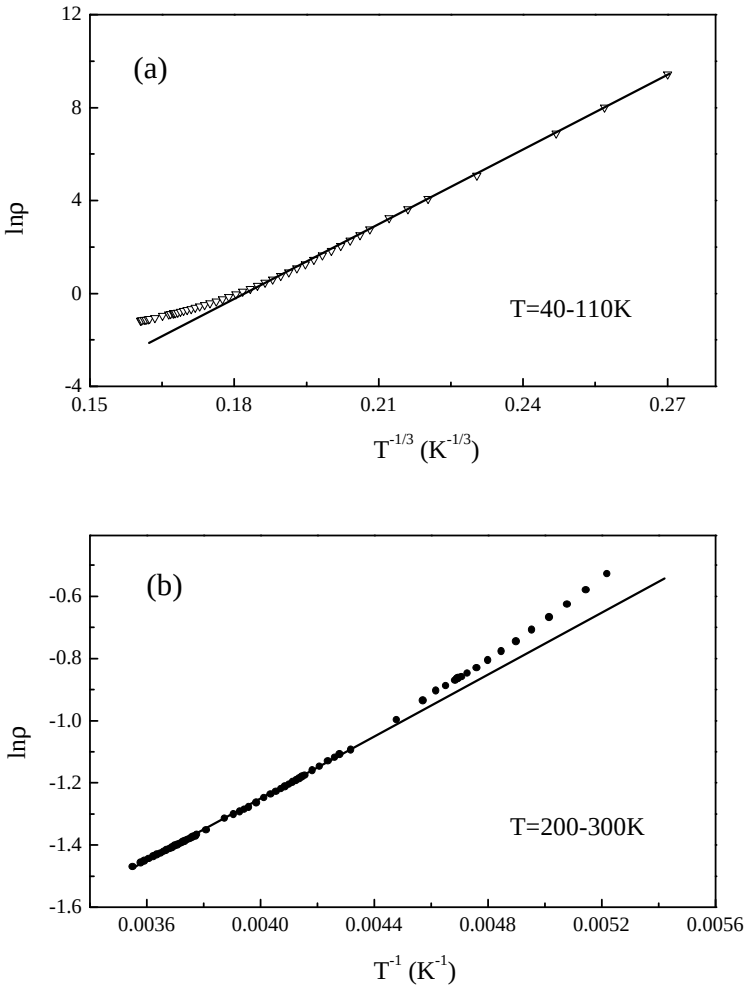

Figure 5. Resistivity ρ as a function of temperature: (a) $\ln\rho$ against $T^{-1/3}$ (the fitted line is for data in the range 40–110 K); (b) $\ln\rho$ against $1/T$ (the fitted line is for data in the range 200–300 K).

for $T < 115$ K the slope of W versus T is positive [24].

A more detailed examination of the temperature dependence of the resistivity shows that between 40 K and 110 K the best fit is given by the two-dimensional version of Mott's variable range hopping (VRH) expression [26] $\rho \propto \exp(T_0/T)^{1/3}$, with $T_0 = 1.25 \times 10^6$ K (see figure 5(a)). Similar values of the characteristic temperature T_0 have been obtained for other manganites where the resistivity is mainly due to three dimensional variable range hopping [27]. The two-dimensional behaviour may be due to confinement of charge carriers to the perovskite layers. Between 115 K and 200 K the temperature dependence of the resistivity does not possess a simple functional form, but between 200 K and 300 K it fits well to a thermally activated conduction law $\rho \propto \exp(E_a/k_B T)$, with $E_a = 42.12$ meV (see figure 5(b)). This is of the same order of magnitude as but somewhat smaller than the values $E_a \sim 100$ meV typically found for the $n = 2$ compounds [8]. Such activated

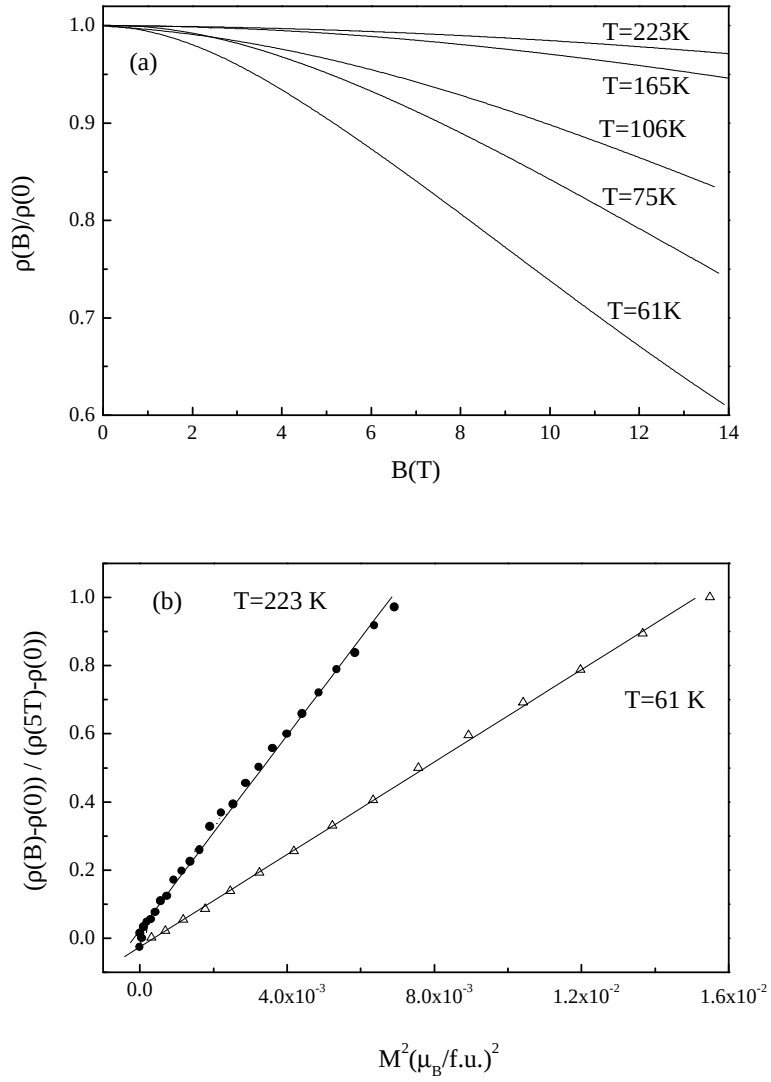

Figure 6. (a) Magnetotransport data for $Ca_4Mn_3O_{10}$ as a function of field for different temperatures. (b) The linear relationship between magnetoresistance and the square of magnetization. The change in resistivity has been normalized to the change in resistivity at 5 T in order to show both data sets more clearly.

transport has been attributed in some CMR materials to the hopping of small polarons [28] or magnetic polarons [1].

The field dependence of the normalized resistivity $\rho(B)/\rho(0)$ for different temperatures is plotted in figure 6(a). We observe no saturation of the resistivity in fields of up to 14 T and conclude that the spins are not fully aligned along the field direction even at 14 T; this is in qualitative agreement with the magnetization, which is far from saturation, even at 5 T.

The magnetoresistance values both in the high and low temperature regions are proportional to the square of magnetization (i.e. $|\Delta\rho/\rho(0)| \propto M^2$, where $\Delta\rho = \{\rho(B) -$

$\rho(0)\}$) over the whole field range for which data are available (see figure 6(b)). This dependence suggests that the mechanism responsible for the magnetoresistive effect is spin-dependent scattering [29], i.e. a bulk, *intrinsic* mechanism due to the reduction in spin disorder caused by the increasing magnetic polarization of the sample as the applied field rises. A similar M^2 dependence has been associated with spin-polarized tunnelling between ferromagnetic grains (i.e. an *extrinsic* effect) [30, 31], but this mechanism is unlikely to be responsible for the magnetoresistance in our compound, which is only very weakly ferromagnetic. Further support for the conclusion that the magnetoresistance is due to spin-dependent scattering comes from the fact that the magnetoresistance does not exhibit any distinct change at $T = 115$ K; the $|\Delta\rho/\rho(0)| \ \alpha \ M^2$ dependence is observed in *both* paramagnetic and magnetically ordered phases. In contrast, granular mechanisms are usually significant *only* in the presence of magnetic order.

In summary, $Ca_4Mn_3O_{10}$ shows a sudden transition to a complicated canted antiferromagnetic ground state at 115 K with a small spontaneous magnetization. The temperature dependence of the resistivity is characteristic of an insulator and the charge transport is only weakly influenced by magnetic effects. This weak magnetoresistance is proportional to the square of the magnetization as expected for spin-dependent scattering.

CMR observed in some $n = \infty$ RP compounds is associated with the development of an ordered ferromagnetic state and in some weakly conducting $n = 2$ compounds with the development of ferromagnetic clusters [10, 23]. In both cases it seems likely that mixed valence–double exchange is involved. The ferromagnetism in such compounds often seems to occur as a result of interactions involving carriers [3], available as a result of doping. The absence of CMR in our more *insulating* compound may be associated with the consequent failure of even incipient ferromagnetism to develop. However, it should be kept in mind that in pyrochlores the observation of CMR does not depend on the mixed valence–double exchange mechanism [14].

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