Multiferroic behavior in the new double-perovskite Lu$_2$MnCoO$_6$

S. Yáñez-Vilar$^1$, E. D. Mun$^2$, V. S. Zapf$^2$, B. G. Ueland$^3$, J. Gardner$^{4,5}$, J. D. Thompson$^3$, J. Singleton$^2$, M. Sánchez-Andújar$^1$, J. Mira$^6$, N. Biskup$^7$, M. A. Señaris-Rodríguez$^1$, C. D. Batista$^8$

$^1$Dpto. Química Fundamental U. Coruña, 15071 A Coruña (Spain)
$^2$National High Magnetic Field Laboratory (NHMFL) Materials Physics and Applications - Condensed Matter and Magnetic Science (MPA-CMMS), Los Alamos National Lab (LANL) Los Alamos NM 98545 (USA)
$^3$MPA-CMMS, LANL, Los Alamos, NM 87545 (USA)
$^4$NIST Center for Neutron Research National Institute of Standards and Technology, 100 Bureau Drive Gaithersburg Maryland 20899 (USA)
$^5$Indiana University, Bloomington, Indiana 47408 (USA)
$^6$Dpto. Física Aplicada U. Santiago de Compostela 15782 Santiago de Compostela (Spain)
$^7$Dpto. Tecnologías de la Información Inst. de Ciencia de Materiales 28040 Madrid (Spain)
$^8$Theory division, LANL, Los Alamos, NM 87545 (USA)

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We present a new member of the multiferroic oxides, Lu$_2$MnCoO$_6$, which we have investigated using X-ray diffraction, neutron diffraction, specific heat, magnetization, electric polarization, and dielectric constant measurements. This material possesses an electric polarization strongly coupled to a net magnetization below 35 K, despite the antiferromagnetic ordering of the $S = 3/2$ Mn$^{4+}$ and Co$^{2+}$ spins in an $↑↑↓↓$ configuration along the c-direction. We discuss the magnetic order in terms of a condensation of domain boundaries between $↑↑$ and $↓↓$ ferromagnetic domains, with each domain boundary producing a net electric polarization due to spatial inversion symmetry breaking. In an applied magnetic field the domain boundaries slide, controlling the size of the net magnetization, electric polarization, and magnetoelectric coupling.

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I. INTRODUCTION

Magneto-electric (ME) multiferroics are materials with long-range electric and magnetic order. Understanding how multiple order parameters coexist and couple is interesting in and of itself. However, ME multiferroics also have potential applications to magnetic storage, novel circuits, sensors, microwave and high-power applications. Achieving strong ME coupling between net magnetization and net electric polarization is particularly important for applications. To date however, multiferroics are rare, and those with significant ME coupling even more so. Transition magnetic oxides have been attracting the most attention in this field recently due to their relatively high magnetic ordering temperatures and tendency to form large electric polarizations. Those with the strongest ME coupling have complex spin textures that break spatial-inversion symmetry (SIS) and alter the lattice so as to generate an electric polarization. The trouble is that many of these complex spin textures don’t produce any net magnetization.

Ca$_3$MnCoO$_6$ was recently found to exhibit a net hysteretic magnetization below 14 K, coupled to a ferroelectric polarization that is suppressed in magnetic fields of 10 T. This compound forms chains of alternating Mn$^{4+}$, $S = 3/2$ and Co$^{2+}$, $S = 1/2$ ions, with the chains in turn arranged in magnetically frustrated triangles. Magnetic exchange is mediated via oxygens that form edge-sharing octahedra around each ion. An $↑↑↓↓$ magnetic structure along Mn-Co chains breaks spatial inversion symmetry and induces electric polarization. Although an $↑↑↓↓$ spin configuration is found in zero magnetic field, a net magnetization with hysteresis is observed in applied magnetic fields.

Here we present results on a new compound, Lu$_2$MnCoO$_6$ in which we also observe $↑↑↓↓$ magnetic order along Co-Mn chains, that creates an electric polarization. We address the issue of how this antiferromagnetic structure can produce a net magnetization. Although the magnetic field-coupled electric polarization of Lu$_2$MnCoO$_6$ is smaller than in Ca$_3$MnCoO$_6$, partially due to its polycrystalline nature, the transition temperature for Lu$_2$MnCoO$_6$ is higher (35 K), and the magnetic
field required to suppress electric polarization is lower (1.2 T), bringing us a step closer to useful temperatures and magnetic fields. The magnetic structure is also simpler with no frustrated triangular arrangement of the Co-Mn chains (see figures 1 and 2), thus unraveling the physics is more straightforward. In Lu₂MnCoO₆, both Co²⁺ and Mn⁴⁺ spins are $S = 3/2$ instead of Co²⁺ $S = 1/2$ and Mn⁴⁺ $S = 3/2$, and the oxygen octahedra are corner-sharing rather than edge-sharing. These suggest that the ↑↑↓↓ magnetic structure coupling to electric polarization can be a wide-spread mechanism for coupling of net magnetism and electric polarization and can be pushed in the direction of useful temperatures and magnetic fields for applications.

II. MATERIALS AND METHODS

We synthesized a polycrystalline sample of Lu₂MnCoO₆ by a nitrate decomposition method using Lu₂O₃ (Aldrich, 99.9%), Co(NO₃)₂·6H₂O (Aldrich, 98%), and Mn(NO₃)₂·5H₂O (Aldrich, 98%) as starting materials. We performed numerous syntheses to obtain a pure sample because there is frequently a small quantity of Lu₂O₃. The procedure was as follows: Lu₂O₃ was first converted into the corresponding nitrate by dissolution in 30% nitric acid. This product was then added to an aqueous solution in which stoichiometric amounts of Mn(NO₃)₂·H₂O and Co(NO₃)₂·6H₂O were also dissolved. The resulting solution was heated at 200 °C until it formed a brown resin, whose organic matter was subsequently decomposed at 400 °C. The obtained precursor powder was then treated at 800 °C/24 h, 1000 °C/24 h, 1100 °C/96 h, 1150 °C/96 h and 1200 °C/48 h with intermediate grindings. The sample was then cooled at 42 °C/hr to room temperature.

The purity of the material was initially checked by conventional X-ray powder diffraction (XRPD) in a Siemens D-5000 diffractometer at room temperature using Cu Kα radiation. Additional studies were carried out with high resolution synchrotron X-ray powder diffraction (SRXPD) in the ID31 beamline ($\lambda = 0.3994$Å) at the European Synchrotron Research Facility (ESRF) in Grenoble, France. For this purpose, the samples were loaded in a borosilicate capillary ($\phi = 0.3$ mm) and rotated during data collection. Rietveld refinements were performed with the Fullprof program suite. The peak shapes were described by a pseudo-Voigt function, the background was modeled with a 6-term polynomial, and in the final steps of the refinement all atomic coordinates and isotropic temperature factors were included. Iodometric titrations were carried out to analyze the oxygen content of the material. The sample was dissolved in acidified KI solutions and the I₂ generated was titrated against a thiosulphate solution. The whole process was carried out under an argon atmosphere. The granulometry of the sample was studied by Scanning Electron Microscopy (SEM), in a JEOL 6400 microscope.

Neutron diffraction measurements were made at the National Institute of Standards and Technology Center for Neutron Research (NCNR) on the BT1 High Resolution Powder Diffractometer. The (311) reflection of Ge or Cu was used to produce monochromatic neutron beams with wavelengths of $\lambda = 2.079$ and 1.540Å, respectively. 15°, 20°, and 7° collimators were used on the in-pile, monochromated, and diffracted beams. The sample was loaded in a V can filled with He exchange gas and mounted in a closed-cycle He refrigerator capable of cooling down to $T = 4$ K. Data were refined using the FullProf program suite and the program k-search was used to help determine the propagation vector of the magnetic order. Representational analysis to determine the symmetry allowed magnetic structures was performed using the programs BasIreps and SARAh. Quoted uncertainties represent one standard deviation.

Pressed pellet samples were used for all the measurements described below.

DC magnetization measurements were made in a Quantum Design (QD) Vibration Sample Magnetometer (VSM) at the National High Magnetic Field Laboratory (NHMFL) in Los Alamos, NM in magnetic fields up to 13 T, with a DSM 1660 VSM in Spain, and with an extraction magnetometer in a "short pulse" magnet (7 ms rise time, 100 ms total pulse time) up to 60 T at the NHMFL. AC magnetometry was measured in a QD AC superconducting quantum interference de-
TABLE I: Structural parameters after the Rietveld refinement of the SXRPD pattern with a monoclinic symmetry (S.G: P2\(^1\)/m) at room temperature. The estimated errors are in parentheses.

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| Lu   | 0.5208(1) | 0.5787(1) | 0.2499(1) |
| Co   | 0   | 0.5 | 0.5 |
| Mn   | 0   | 0   | 0   |
| O1   | 0.3841(16) | 0.9585(17) | 0.2411(16) |
| O2   | 0.1971(20) | 0.1957(25) | -0.0575(15) |
| O3   | 0.3228(18) | 0.6953(21) | -0.0593(14) |
| \(R_{wp}\) | 14.8 | \(R_p\) = 8.05 | \(\chi^2\) = 1.87 |

TABLE II: Mn-O and Co-O bond distances and Mn-O-Co angles obtained from the room temperature refinement. Valences derived from the Bond Valence Sum (BVS) method for Mn and Co atoms are also shown. The estimated errors are in parentheses.

| BVS: Mn valence +3.61, Co valence +2.38, Mn valence +3.61 | distances (\(\text{Å}\)) | angles (deg) |
|----------------------------------------------------------|--------------------------|-------------|
| Co-O(1)                                                  | 2.020(12)                | Mn-O(1)-Co | 141.8(3) |
| Co-O(2)                                                  | 2.014(15)                | Mn-O(2)-Co | 145.4(6) |
| Co-O(3)                                                  | 2.033(10)                | Mn-O(3)-Co | 142.9(4) |
| Mn-O(1)                                                  | 1.897(12)                |             |           |
| Mn-O(2)                                                  | 1.955(13)                |             |           |
| Mn-O(3)                                                  | 1.974(11)                |             |           |

III. RESULTS

A. Crystal structure from X-ray diffraction

Both neutron and X-ray diffraction measurements show that this sample is single phase and can be indexed in the monoclinic space group P2\(^1\)/m (see figure 2). The results of the iodometric titrations indicate that the sample has a very small oxygen deficiency (\(\delta\)) of 0.02. Scanning electron micrographs show that the morphology and microstructure of the sample consists of sintered particles with an average diameter \(\phi \approx 2\mu\). The room temperature SXRPD pattern along with its refinement are shown in figure 3. Following the structure determined for La\(_2\)MnCoO\(_6\)\(^{20}\) and a model proposed for Y\(_2\)MnCoO\(_6\)\(^{21}\), the constraint of complete transition metal cationic ordering was imposed to this refinement (Wyckoff positions 2c and 2b sites for the Mn and Co cations, respectively). However, as shown in the next section, our neutron diffraction data indicate that 9% mixing occurs between the sites.

Dielectric measurements in magnetic fields up to 14 T were performed at various temperatures for frequencies between 10 kHz and 1 MHz. The sample used for these measurements had an area of 26 mm\(^2\) and a thickness of 0.8 mm. Gold was deposited on the surfaces to ensure good electrical contact.

B. Magnetic structure from powder neutron diffraction

Neutron diffraction data taken at \(T = 100\) and 4 K in zero magnetic field are shown in figure 3a and b, respectively. Data at 100 K correspond to the crystal structure of the lattice and yield lattice parameters similar to those determined from the X-ray diffraction results presented above. However, the difference in the neutron scattering lengths for Co and Mn allows us to determine that the 2c sites are occupied by 91(2)% Co and 9(2)% Mn, and that the 2d site are occupied by 94(2)% Mn and 6(2)% Co. The “goodness of fit” indicators for figure 3a are \(R_{wp} = 7.46\)% and \(\chi^2 = 0.75\). Figure 4 shows data at
FIG. 4: Elastic neutron diffraction data for polycrystalline Lu$_2$MnCoO$_6$ at 100 K (a) and 4 K (b). The main panels show data taken with $\lambda = 1.540$ Å neutrons, while the inset to figure b shows data taken with $\lambda = 2.079$ Å neutrons. Red circles are experimental data, and the blue lines are fits to the data from Rietveld refinements. Ticks underneath the data indicate symmetry-allowed Bragg positions, and purple lines beneath the ticks show the differences between the data and fits.

$T = 4$ K containing Bragg peaks from both the crystal structure and magnetic order. We determined the magnetic order from the $\lambda = 2.079$ Å data, part of which is shown in the inset to figure b, since the higher wavelength neutrons provide greater resolution at lower values of momentum transfer $Q$. In figure b we include the $\lambda = 1.540$ Å data and its refinement for easy comparison to figure a. After an exhaustive search we determined $\vec{k} = (0.0223(8), 0.0098(7), 0.5)$ as the propagation vector of the AFM order. This vector is only slightly incommensurate in the $a$ and $b$ directions, but the incommensurability is necessary to fit all of the magnetic peaks. For example, the magnetic peak shown in the inset to figure b at 33.5° cannot be fit without allowing $\vec{k}$ to be incommensurate in both the $a$ and $b$ directions. The derived magnetic structure is shown in figure 1 and consists of an $\uparrow\uparrow\downarrow\downarrow$ type magnetic order with magnetic moments of $2.56(7)$ $\mu_B$/Co and $2.56(7)$ $\mu_B$/Mn pointed along the $c$-axis. We note that the moments for the Co and Mn ions were not constrained to be equal during the refinement. The "goodness of fit" indicators for the inset to figure a are $R_{wp} = 4.65\%$ and $\chi^2 = 1.83$.

C. Thermodynamic measurements

The specific heat data in figure 5 shows a peak consistent with the onset of magnetic order below $\sim 43$ K in a polycrystalline sample. In magnetic fields up to 13 T, this peak broadens and shifts to higher temperature. This data is the total specific heat including magnetic and phonon contributions, which could not be easily subtracted.

Figure 6a shows the DC magnetization vs temperature $M(T)$ measured on warming in a 0.1 T, after either magnetic field cooling (FC) in a 0.1 T magnetic field or zero magnetic field cooling (ZFC) from room temperature. A kink is observed in the magnetization near 43 K and the ZFC and FC curves separate below $\sim 35$ K with the ZFC curve peaking at 20 K and then dropping to zero. The inset to figure 6a shows the inverse susceptibility vs temperature with a fit to the Curie-Weiss law above 150 K. The fit results in
a Curie-Weiss temperature of 58 K and an effective moment of 5.5 $\mu_B$/formula unit, which is roughly consistent with one $S = 3/2$ Co$^{2+}$ and one $S = 3/2$ Mn$^{2+}$ spin per formula unit. AC susceptibility $\chi_{ac}$ data taken at $\sim 10$, 100, and 1000 Hz as a function of temperature is shown in figure 6b. $\chi_{ac}(T)$ shows a frequency-independent peak (within the resolution of the experiment) at 43.5 K indicating that a transition to long range magnetic order occurs. Below 35 K, the ac susceptibility shows a small frequency-dependence indicative of slow spin dynamics. The onset of the frequency dependence arises at the same temperature below which a bifurcation between the ZFC and FC $M(T)$ curves occurs. Though not shown here, the ZFC magnetization relaxes in the direction of the FC magnetization with a time constant of a few hours. The observed slow spin dynamics are reminiscent of spin glass type behavior occurring below 35 K.

Magnetization vs magnetic field $M(H)$ hysteresis curves are shown in figure 7a. at 2, 3, and 4 K for magnetic fields up to 13 T. At 2 K, ferromagnetic-like hysteresis is observed, with a very sudden switching of the magnetization occurring at a coercive magnetic field of 1.21 T. A plateau-like feature is seen between 1.2 and 3 T, as indicated with arrows. The switching behavior of the magnetization broadens in $H$ for the data at 3 and 4 K and the plateau disappears. The magnetization does not fully saturate by 13 T; a moment 4.5 $\mu_B$ is achieved at 2 K and 13 T. Hysteresis curves to higher magnetic fields were measured in pulsed magnetic fields up to 60 T at the NHMFL, as shown in figure 7b. This pulsed magnetic field data shows that the expected full moment of $\sim 6 \mu_B$ is achieved by 0.5 K and 60 T, which would be expected from the combined Mn$^{2+}$ $S = 3/2$ and Co$^{2+}$ $S = 3/2$ moments (neglecting orbital effects). Thin arrows indicate a slight plateau in the magnetization.
The change in electric polarization with magnetic field $\Delta P(H)$ was measured in pulsed magnetic fields up to 60 T after electrically poling the sample by first cooling the sample from 70 to 4 K in an electric field and then removing the electric field and shorting the two sides of the sample before measuring. Poling electric fields of 2 MV/m were used for the data shown, and $\Delta P(H)$ was found to be linear for poling electric fields between 0 and 2.5 MV/m. The measured signal, $dP(H)/dt$, and the integrated $\Delta P(H)$ are shown in figure 8b. The measured $\Delta P$ is constant for magnetic fields between 0 and 1.6 T (2.6 T below 1.5 K), then drops suddenly and continues to drop at a slow and continuous rate up to 60 T (see inset). On the downsweep of the magnetic field and on subsequent $\Delta P(H)$ measurements we observe almost no $H$-dependence (the second shot after poling shows 2% of the original $\Delta P(H)$, and subsequent shots show no resolvable $\Delta P(H)$). A significant $\Delta P(H)$ can only be observed again after re-poling. We interpret this as a magnetic field-induced suppression of most of the electric polarization. $\Delta P(H)$ was measured for both $\vec{P}$ parallel and perpendicular to $\vec{H}$ and the same results were found in these polycrystalline samples. Data for both magnetic field directions at 4 K and up to 60 T are shown in the inset to figure 8a. All the rest of the data shown was measured with $\vec{P} \parallel \vec{H}$. The inset to figure 8a shows the temperature dependence of $\Delta P$ between $\mu_0 H = 0$ and 15 T. The onset of $\Delta P(H)$ occurs around 30 K.

The dielectric constant as a function of temperature and magnetic field is shown in figure 9, for frequencies of 10 kHz and 1 MHz. It exhibits a broad peak near 35 K, which is the same temperature below which splitting between the ZFC and FC magnetization curves arises, frequency dependence of the ac susceptibility occurs, and $\Delta P(H)$ becomes nonzero. The peak in the dielectric constant is completely suppressed in an applied magnetic field of 14 T.

**IV. DISCUSSION**

We interpret our results as follows: below 43 K, long-range magnetic order sets in, observed as a significant kink in the magnetization and a peak in the specific heat. Below 35 K, an electric polarization can be induced by poling in an electric field, and glassy magnetic dynamics and a hysteretic magnetization also occur. Consistent with this picture, a peak in the dielectric constant appears near 35 K (see figure 9). Neutron diffraction data at 4 K and $\mu_0 H = 0$ identify a ferroelectric $\uparrow\downarrow\downarrow\downarrow$ configuration of spins along chains of alternating $S = 3/2$ Mn$^{4+}$ and $S = 3/2$ Co$^{2+}$ spins in the $c$-axis (see figure 1). This spin configuration is likely the result of frustration between nearest-neighbor and next-nearest-neighbor magnetic exchange interactions with opposite sign, similar to Ca$_3$MnCoO$_6$.

In the following we use the term “domain boundary” to refer to the boundary between $\uparrow\uparrow\downarrow\downarrow$ and $\downarrow\downarrow\downarrow\downarrow$ spins along the $c$-axis. Since there are two types of ions (Co$^{2+}$ and Mn$^{4+}$), there are also two types of domain walls: the ones that are centered on a Co$^{2+}$-Mn$^{4+}$ bond and the ones centered on a Mn$^{4+}$-Co$^{2+}$ bond. These different domain walls carry opposite electric po-
larizations because they break the local spatial inversion symmetry in opposite ways. In other words, the ferromagnetic domains walls carry an internal degree of freedom of electric polarization due to the small structural distortions caused by the magnetostriiction effects induced by the wall. This leads to the coupling between magnetism and ferroelectricity. In particular, a perfect $\uparrow\uparrow\downarrow\downarrow$ phase can be thought of as a condensation of domain walls whose electric polarizations are all aligned. If the sample is cooled through its transition in an electric field, it stores a net electric polarization by inducing more domains with one polarization than with the opposite. This electric polarization is mostly destroyed in applied magnetic fields above 1.5 T, with an additional small electric polarization persisting to 60 T. Once destroyed, the sample must be re-poled (cooled again through $T_c$ in an electric field) to regenerate the maximum electric polarization. The dielectric constant measurements also confirm the strongly magnetic field-dependent nature of the electric polarization, with the peak near 35 K completely suppressed in applied magnetic fields of 14 T.

While the $\uparrow\uparrow\downarrow\downarrow$ spin configuration does not produce a net magnetization, we suggest that in applied magnetic fields the domain walls slide apart due to the close proximity to a ferromagnetic instability. As the domain walls become less dense, the electric polarization is also suppressed. Commensurate configurations such as $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$ might lock in, resulting in plateaus in the magnetization. One plateau is observed near 1/3 saturation magnetization at 2 K. Magnetization data on single crystals as well as neutron diffraction data in magnetic fields are needed to test this scenario.

We note that the condensation of domain walls in the $\uparrow\uparrow\downarrow\downarrow$ leads to infinitely small domain walls and the domains themselves are as small as 7 Angstroms (c-axis lattice parameter). By contrast, conventional domain walls induced by dipole-dipole interaction in ferromagnets and multiferroics can be tens to hundreds of nm wide with domains that can be up to hundreds of mm wide. In Lu$_2$MnCoO$_6$, the condensation of domain walls that leads to the $\uparrow\uparrow\downarrow\downarrow$ configuration likely results from frustration between nearest and next-nearest neighbor interactions. Consequently, in comparison to conventional ferromagnets, the domain walls in Lu$_2$MnCoO$_6$ are far smaller and also more mobile due to the proximity to a ferromagnetic instability. This increased mobility may account for the spin glass-like frequency-dependence of the ac susceptibility below 35 K. An alternate explanation for the net hysteretic magnetization in magnetic fields is that spins tilt out of the c-axis. However this is less likely to fully explain the hysteresis and slow relaxation of the magnetization.

Although the coercive magnetic field for switching the magnetization is 1.21 T and most of the electric polarization is destroyed at 1.6 T, saturation magnetization is not reached until ~ 60 T, and the electric polarization continues to show a small net contribution up to this magnetic field. A likely explanation is that the 9% Mn-Co site interchange determined from the neutron scattering data results in some Mn-Mn and Co-Co nearest neighbor pairs. In related compounds, Co-Co and Mn-Mn nearest neighbor superexchange interactions are antiferromagnetic, thus they would locally pin the domain boundaries between “up” and “down” regions of spins.

Finally we should mention that Lu$_2$MnCoO$_6$ is another close relative of Lu$_2$MnCoO$_6$ that has been studied since the 1950s. In this material, confusion reigned for a long time due to the presence of multiple phases with different Mn and Co valences, as well as Mn-Co site interchange. These problems resulted in different magnetic ordering temperatures, saturated moments, and different degrees of ferroelectric power. These structural problems mostly ensued when the oxygen deficiency $\delta$ was greater than 0.02, allowing Co$^{3+}$ and Mn$^{3+}$ to form, as well as from Mn-Co site interchange. In the case of our Lu$_2$MnCoO$_6$, we see only one magnetic phase and iodometric titrations indicate that $\delta \sim 0.02$. We do however see Co-Mn site interchange of about 9%, which could create local antiferromagnetic interactions as discussed.

V. CONCLUSION

In summary, Lu$_2$MnCoO$_6$ is a new member of the multiferroic oxides, showing magnetic order below 43 K, and ferroelectricity below 35 K that is strongly coupled to a net magnetism. An $\uparrow\uparrow\downarrow\downarrow$ arrangement of the spins in zero magnetic field breaks spatial inversion symmetry and induces electric polarization. We suggest that the domain walls between $\uparrow\uparrow$ and $\downarrow\downarrow$ regions slide in an applied magnetic field due to close proximity to a ferromagnetic instability, resulting in net ferromagnetic-like magnetization with a coercive field of 1.21 T that switches between states of approximately 1/3 saturation magnetization. A magnetization of $\sim 6 \mu_B$/formula unit is eventually reached by 60 T consistent with the $S = 3/2$ spin for both Co$^{2+}$ and Mn$^{4+}$ ions. The electric polarization is strongly suppressed in magnetic fields above 1.6 T and the magnetic field-induced polarization change is $\sim 2 \mu C/m^2$.

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