Nickel-Titanium double perovskite: A three-dimensional spin-1 Heisenberg antiferromagnet

M. Karolak, M. Edelmann and G. Sangiovanni
Institut für Theoretische Physik und Astrophysik,
Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
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The double perovskite La$_2$NiTiO$_6$ is identified as a three-dimensional $S$=1 quantum magnet. By means of Density Functional Theory we demonstrate that this material is a high-spin $d$-electron system deep in the Heisenberg limit and establish that its paramagnetic Mott phase persists down to low temperatures ($T_N$=25K) not because of frustration effects but rather for the extreme strong coupling physics. Our many-body calculations on an ab initio-derived multi-orbital basis predict indeed a kinetic energy gain when entering the magnetically ordered phase. La$_2$NiTiO$_6$ emerges thus as a paradigmatic realization of a spin-triplet Mott insulator. Its peculiar properties may turn out to be instrumental in the ongoing chase after correlated topological states of matter.

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Introduction. Nickel (Ni) in $d^8$ configuration has been attracting growing attention for the possibility to realize the “Haldane” $S$=1 spin-chain [1,2]. In compounds like CsNiCl$_3$ or NiTa$_2$O$_6$ the Ni atoms are connected via small hopping integrals $t$ along specific one-dimensional paths and charge fluctuations are strongly suppressed by the large on-site Hubbard repulsion $U$. This allows for a theoretical description in terms of the 1D-Heisenberg model with an antiferromagnetic superexchange coupling $J \propto t^2/U$. In two dimensions the interest in $S$=1 quantum antiferromagnets has been somewhat hidden by the widely investigated spin-1/2 $t$-$J$ model, related to the physics of underdoped high-$T_c$ cuprates. Ni is again present in some of the $S$=1 bulk materials with strong 2D character, such as La$_2$NiO$_4$ or K$_2$NiF$_4$ [6,7]. In an interesting recent proposal Chen, et al. suggested to artificially design a 2D spin-1 Mott insulator upon heterostructuring Ni and Ti single perovskites [12].

In 3D spin-1 quantum magnets are found in pyrochlore compounds, such as ZnV$_2$O$_4$ or MgV$_2$O$_4$ [13,14], where the absence of magnetic ordering down to very low temperatures is however due to frustration rather than to the large $U$. Face-centered cubic (fcc) $S$=1 materials such as NiS$_2$ and NiO [15,16] are sometimes described in terms of spin-only models with nearest- (90°) and next-nearest (180°) exchange couplings $J_1$ and $J_2$, respectively. Yet, these systems as well as the $d^2$-vanadates [19] are quite far from the strong-coupling Heisenberg limit, because the hybridization between the transition-metal ion and the “bridging” ligand atoms is significant. Charge fluctuations indeed still play a role, as also testified by the relevant $d$-bandwidth which in these compounds hardly gets smaller than ~1.5-2.0 eV. In fact, what has not been identified so far is a 3D spin-1 compound for which the combination of small hoppings and large $U$ leads to tiny exchange amplitudes, i.e. a strong-coupling Heisenberg antiferromagnet for which long-range order is suppressed by strong local fluctuations of the order parameter.

Here we demonstrate that the Nickel double perovskite La$_2$NiTiO$_6$ is a perfect realization of a $S$=1 quantum antiferromagnet, far into the Heisenberg limit, with $J_2 \gg J_1$, i.e. living on an unfrustrated three-dimensional fcc lattice [20,21]. We derive the low-energy Heisenberg model ab initio and establish that the relevant superexchange scales are very small ($J_2 \sim$1.6 meV). In order to fully describe the residual charge fluctuations, which in spin-1 systems may be relevant due to the importance of biquadratic effects as well as three-body interactions [25,26], we also go beyond the bilinear spin-only description and investigate the antiferromagnetic (AFM) phase in the “full” Hubbard model. This allows us to make a thermodynamic analysis of La$_2$NiTiO$_6$ revealing the kinetic energy-driven ordering mechanism.

La$_2$NiTiO$_6$ is not only interesting for its magnetically ordered phase, but also for the particularly low value of the Néel temperature $T_N$. As a consequence, the paramagnetic insulating state exists in a huge range of temperatures. Even though its properties as a Mott insulator have not been discussed hitherto, it is important to stress that La$_2$NiTiO$_6$ can actually be synthesized, as described in the few existing chemistry reports [27-31]. Here we connect its unique features as a high-spin paramagnet with the peculiar electronic structure: a half-filled $e_g$-manifold at the Fermi level which is extremely narrow and uncommonly well separated from any other band. The origin of this lies in the isotropic reduction of the hoppings in all three spatial directions, something hardly possible to achieve artificially but that nature does very effectively, replacing the Ni-O-Ni bonds characteristic of other $S$=1 materials with longer Ni-O-Ti-O-Ni ones. This class of $d^2$-$d^0$ double perovskites can open new directions in oxide engineering: by considering also heavier elements of the Ni-group and upon splitting the $e_g$ bands by heterostructuring or strain a correlation-driven band-inversion can be realized, as in recent theoretical proposals for interacting topological insulators [32,33].
Ni-Ni hopping is small, the bridization to O and Ti, are shown in Tab. I. The overall bandwidth of the O 2$p$ states have been used (see Supplemental Material). The thickness of the bands denotes the corresponding orbital character.

The electronic structure. La$_2$NiTiO$_6$ crystallizes in a double perovskite structure with a small monoclinic distortion (P2$_1$/n space group), as determined from neutron powder diffraction experiments [23,31]. Structural relaxation within Density Functional Theory (DFT) using the GGA(PBE) [37] functional results only in minor changes to the experimentally measured structure. The Ni/TiO$_6$ octahedra display a very small Jahn-Teller distortion (the length of the Ni/Ti-O bonds differ by at most 0.4%) and show an alternating tilting.

For the paramagnetic calculations we consider a unit cell containing two formula units whereas the magnetic relaxations are described for a cell with two (locally equivalent) Ni. For (b) and (c) maximally-localized Wannier functions spanning Ni $d$, Ti $t_{2g}$ and O $p$ states have been used (see Supplemental Material). The thickness of the bands denotes the corresponding orbital character.

**FIG. 1.** (color online) (a) Crystal structure of La$_2$NiTiO$_6$. (b) Density of states (Fermi level at $E=0$). (c) Electronic structure for a cell with two (locally equivalent) Ni. For (b) and (c) maximally-localized Wannier functions spanning Ni $d$, Ti $t_{2g}$ and O $p$ states have been used (see Supplemental Material). The thickness of the bands denotes the corresponding orbital character.

**Electronic structure.** The electronic band structure calculated with GGA using the VASP code [38] and the density of states for Ni $d$, Ti $t_{2g}$ and O $p$ bands are shown in Fig. 1: and b, respectively. Nominally Ni is in a $d^8$ configuration and Ti in $d^3$. In DFT La$_2$NiTiO$_6$ is a metal, with two degenerate Ni $e_g$ bands crossing the Fermi level. Due to the presence of the inactive Ti “spacers” the Ni $e_g$ bands are remarkably narrow. The corresponding value of the bandwidth $W_{e_g} \sim 0.8$ eV is indeed substantially smaller than that of Ni$_2$O$_2$ [17,39,40], of NiO [41], and of other high-spin three-dimensional compounds [42]. The $t_{2g}$ manifold of Ni lies 1 eV below the Fermi level and, approximately 1 eV further below one finds the upper edge of the O 2$p$ bands.

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We extracted maximally-localized Wannier functions [43] spanning the two Ni $e_g$-states using the Wannier90 package [44]. The calculated Ni-Ni hopping amplitudes for the $3z^2-r^2$ (in the following abbreviated as $z^2$) and $x^2-y^2$-like orbitals, effectively containing the hybridization to O and Ti, are shown in Tab. I. The overall Ni-Ni hopping is small, the $t_{2g}$ along the $c$ axis being the largest one ($-97$ meV). Along the same direction the $x^2-y^2$ hardly contributes. In the $ab$-plane the situation is more evenly distributed among the two orbitals but the sum of the squares of all hoppings is similar to the same quantity along $c$ (as we will see below $\sum_{mm'}|t_{mm'}|^2$ determines the super-exchange coupling). For Ni-Ni 90° bonds one has two possibilities, either inter- or intra-sublattice hoppings, i.e. either Ni1-Ni2 or Ni1-Ni1, respectively.

The most important outcome of the Wannier projection is that the Ni-Ni 180° hoppings are a factor of 4 to 10 larger than the 90° ones, the latter taking Ni-O-Ti-O-Ni as well as Ni-O-O-Ni paths into account.

**Spin-only model.** The Wannier projection allows us to derive a bilinear Heisenberg Hamiltonian, with which we can give a first description of the physics of La$_2$NiTiO$_6$. To this aim, we downfold [45,46] our ab initio $e_g$-model with two electrons onto the subspace of singly occupied orbitals. The intermediate configurations generated by one Ni-Ni hopping process contain only one intra-orbital double occupation, as sketched in Fig. 2. We considered a local interaction term of Kanamori type [47,48], with an intra-orbital Hubbard repulsion $U$ and a Hund’s cou-

| $t_{mm'}$ [meV] | $z^2$-diag | off-diag | $x^2-y^2$-diag | $10^4|t_{mm'}|^2$ |
|----------------|-------------|---------|----------------|----------------|
| 180° $c$      | -97         | -3/3    | 0              | 9.4            |
| 180° $ab$     | -27         | 44/44   | -70            | 9.5            |
| 90° $ab$      | 11          | 2/2     | -46            | 2.2            |
| 90° $ab$  $c$ | 27          | 25/-19  | -4             | 1.7            |

**TABLE I.** Most representative hopping amplitudes for the Nickel $e_g$-only model of La$_2$NiTiO$_6$. The first two rows represent 180° bonds (i.e. second-nearest neighbors). The third and fourth rows contain 90° bonds (i.e. nearest neighbors) on the same and on different $ab$-planes, respectively. The complete list of hoppings can be found in the Supplemental material.
Hamiltonian reads

$$\mathcal{H}_{\text{Heis}} = \frac{1}{U + J_H} \sum_{m \neq m'} |t_{mm'}|^2 \sum_{ij} \left( \hat{S}_i \cdot \hat{S}_j - 1 \right).$$

One of the processes responsible for the spin-off-diagonal terms is shown in Fig. 4 where also the energies of the initial/final and intermediate states are given. The initial and intermediate configurations are eigenstates of the Kanamori Hamiltonian. The final state is actually the triplet combination which, for simplicity, is represented as just one state in our sketch.

![Figure 2](image.png)

**FIG. 2.** (color online) Sketch of a spin-spin off-diagonal term of $\mathcal{H}_{\text{Heis}}$ between neighboring sites $i$ and $j$. Even though the two $e_g$-orbitals are shown, for the sake of clarity, on two different levels, we stress that they are in fact degenerate.

Using typical interaction values for Ni ($U = 5$ eV and $J_H = 0.8$ eV [52]) we get $J_2 \approx 1.6$ meV and $J_1 \approx 0.3$ meV (or smaller, depending on which 90° bond is considered). This small value of the ratio $J_1/J_2 \approx 0.2$ – a direct consequence of the small nearest-neighbor hoppings – corresponds to a very weak degree of frustration. The 180° Ni-Ni bonds are not strongly disturbed by the nearest-neighbor ones and form four interpenetrating antiferromagnetic simple cubic sublattices. The wave vector of this so-called AF-II phase, which in mean-field is stable for $J_1 < 2J_2$, is $[1/2,1/2,1/2]$. We have performed GGA+U calculations and found that the AF-II order has indeed the lowest energy, in agreement with experiments [24].

**DFT+DMFT calculation.** In order to go beyond the spin-only bilinear Heisenberg model above, we solve the “full” multi-orbital Hubbard model in the Wannier basis using DMFT. In the following we present calculations for the $e_g$-only basis with the SU(2)-symmetric Kanamori interaction. The result is that La$_2$NiTiO$_6$ is a Mott insulator in DFT+DMFT. We have also tried larger basis-sets, in particular a $dp$-model containing Ni $e_g$, Ni $t_{2g}$ and O $p$ bands. The DFT+DMFT result turns out to be robust against the different choices of Wannier projection, in contrast to many other transition-metal oxides for which DFT+DMFT gives qualitatively different outcomes depending on the basis set [19]. We note in passing that this robustness of La$_2$NiTiO$_6$ against the choice of basis set, makes it an ideal testbed material for the derivation of low-energy models for $e_g$-orbitals, in the same way as SrVO$_3$ is very often used for $t_{2g}$ bands. La$_2$NiTiO$_6$ has the additional interesting property of a much stronger effect of the Hund coupling $J_H$ because of the half-filled and the very narrow $e_g$ bands.

The DFT+DMFT solution of La$_2$NiTiO$_6$ for the $e_g$-only model demonstrates that, in a wide range of interaction parameters relevant for Ni ($U=4-7$ eV and $J_H=0.6-1.0$ eV), the local moment is very close to the maximum value of $S_{\text{eff}}=1$. By calculating $\langle S^2 \rangle$ we indeed find its maximum value of 2/3, because the inter-orbital “Hund” double occupancies $d_{\text{Hund}}=(n_1,t_2g)$ and the “anti-Hund” ones $d_{\text{anti-\text{Hund}}}=\langle n_1,t_2g \rangle$ are given by their “saturation” values of 1/3 and 1/6, respectively (see also Fig. 3). In the paramagnetic phase we therefore have $\langle S^2 \rangle = 3\langle S^2 \rangle_1 = 2 = S_{\text{eff}}(S_{\text{eff}}+1)$ with the SU(2)-symmetric Kanamori interaction. Hence $S_{\text{eff}}=1$ and, correspondingly, the local moment is $m \approx 2.83\mu_B$.

So far we have used DFT+DMFT to analyze the paramagnetic phase of La$_2$NiTiO$_6$. Being a mean-field theory, DMFT allows us to follow it down to zero temperature or, alternatively, to calculate the Néel temperature and switch to the magnetically ordered solution below $T_N$. The values of $T_N$ calculated in our ab initio $e_g$-only model for different values of $U$ are shown by the full and empty diamonds in Fig. 3 for $J_H=0.6$ and 1.0 eV, respectively. $T_N$ is in the range 50-70K. Before making a quantitative comparison with the experimental result of 25K we have to consider a reduction of $T_N$ due to 3D spatial fluctuations at finite temperature which are not included in DMFT [54]. In order to quantify their effect we can rely on random-phase calculations and on spin-wave theory (we are not aware of quantum Monte-Carlo results for spin-1 fcc lattices). For our value of the $J_1/J_2$ ratio the random-phase approximation predicts a reduction of $T_N$ of about 35% compared to mean-field [20]. The solid green line in Fig. 3, which takes into account this reduction, is remarkably close to the experimental value. The most plausible reason for an additional reduction of the theoretical $T_N$ is the presence of a few percent of Ni-Ti anti-site disorder, as reported in [24, 31].

In order to prove that La$_2$NiTiO$_6$ is actually a strong-coupling Heisenberg antiferromagnet we perform a thermodynamic analysis. The smoking gun ruling out possible intermediate-coupling physics is a lower total energy for the AFM phase realized through a kinetic energy gain and a loss in potential energy [51, 56, 57, 62]. Our results very clearly indicate a kinetic energy gain, as shown in Fig. 3b. This is calculated from the first moment of $h(k)$, the histogram of the expansion order
FIG. 3. (color online) Energetic balance for $U = 4$ eV, $J_H = 0.6$ eV and $\beta = 200$ (eV)$^{-1}$. (a) Different contributions to the potential energy of the paramagnetic and antiferromagnetic phases (red dots and blue squares, respectively). The error bars are not visible as they are smaller than the symbol size. The potential energy of the AFM solution is larger than that of the PM one (potential energy loss). (b) Histogram of the expansion order of the QMC diagrams contributing to the fermionic trace for the two phases. Its average is proportional to the kinetic energy. The shift towards higher expansion orders for the AFM solution indicates a kinetic energy gain. In (c) $T_N$ calculated within DFT+DMFT for the $e_g$-only model is reported with diamonds (full and empty symbols correspond to $J_H = 0.6$ and 1.0 eV, respectively). Fits to the data (black solid lines) yield a prefactor of the $1/(U+J_H)$ behavior which is very close to the estimate obtained from the mean-field solution of a Heisenberg model with the hopping values from Table I (black dashed line, for $J_H = 1.0$ eV). From Ref. 20 we estimated the reduction of the mean-field value, due to spatial fluctuations (green line).

of the continuous-time hybridization-expansion quantum Monte-Carlo solver [53, 54]. A shift toward larger expansion orders indicates a gain in kinetic energy for the AFM phase ($\Delta E_{\text{kin}} < 0$). At the same time, as shown in Fig. 3, where the local terms of the multi-orbital Hubbard Hamiltonian are separately analyzed, we detect a potential energy loss ($\Delta E_{\text{pot}} > 0$), ruling out intermediate-coupling physics. Our analysis reveals that the potential energy loss is almost entirely given by the corresponding increase in $d_U$, the intra-orbital double occupancies [53], by going from PM to AFM. This is a precise consequence of the strong-coupling physics: the disordered phase has preformed localized moments that slightly delocalize upon entering the ordered phase because they gain coherence [50].

Conclusions. We have shown that La$_2$NiTiO$_6$ is a Hund’s coupling-“assisted” Mott insulator, far in the strong-coupling limit. The peculiar properties of this double perovskite come from the presence of inactive $d^9$ Ti-“spacers” which enlarge the Ni-Ni bonds isotropically in all directions, drastically reducing the relevant bandwidth. The proper low-energy spin-spin model is a Heisenberg Hamiltonian with next-nearest-neighbor exchange coupling $J_2$ equal to about 1.6 meV and nearest-neighbor coupling $J_1$ a factor of 4-5 smaller. On an fcc lattice like the present one, this implies that frustration effects are almost absent and the very low value of $T_N$ is a consequence of the strong local fluctuations of the order parameter. We demonstrate the strong coupling nature of La$_2$NiTiO$_6$ by a direct analysis of the energetic balance within DFT+DMFT. This prediction can be tested, for instance, by looking for the presence of spin-polarons in photoemission as well as in optical conductivity measurements [60-62] which should be visible due to the pronounced three-dimensional character.

Our results unveil a new family of double perovskites – La$_2$NiTiO$_6$ being its first member – that, due to the dramatic reduction of the bandwidth can be very interesting for oxide engineering. One promising direction is to try to split the two $e_g$ bands with strain or upon heterostructuring. This can be achieved because, despite the very isotropic $J_2$, the 180° hoppings of the $z^2$- and of the $x^2-y^2$-orbitals are not symmetric under rotations of the crystal axes. It should therefore be possible to induce a splitting which, due to the hybridization between the two $e_g$-orbitals, may result in a gap of inverted orbital character at specific points of the Brillouin zone. The resulting band structure can in fact be the ideal one for the realization of a correlated topological insulator, with two $d$-electrons in two entangled orbitals forming a large local moment (hence more easily detectable in an experiment). If the $x^2-y^2/z^2$ splitting turns out to be externally tunable, this class of $d^8$-$d^9$ double perovskites could become tremendously attractive from this point of view. By substituting Ni with heavier iso electronic elements the spin-orbit coupling can also concur in the opening of the hybridization gap necessary to realize a correlated topological insulator.

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As shown in Fig. 6, the “Hund” inter-orbital double occupancies $d_H$ (proportional to $U-3J_H$), the “anti-Hund” ones, $d_{anti-H}$ ($\propto U-2J_H$) and the “spin-flip” term $\propto -J_H$ are, close to compensating each other. Since the pair-hopping terms hardly contribute, the potential energy loss reads $\Delta E_{pot}=2\left[(U-3J_H)d_H+J_Hd_{anti-H}+J_Hd_H+J_H\Delta S+U\Delta d_H\right]$ and it is almost entirely given by the corresponding change in $d_H$, the intra-orbital double occupancies: $\Delta E_{pot}=2Ud_H$. At the same time, the length of the (unordered) local moment (whose square is $\propto \langle S^2 \rangle$) changes only slightly by going from the PM to the AFM phase: the latter is
~ 0.002µB shorter than the former. \( \langle S^2_z \rangle = \frac{1}{4} \langle n_{\text{tot}} \rangle - d_U + d_H - d_{\text{anti-H}} \)
\( \langle S^2_x \rangle = \frac{1}{4} \langle n_{\text{tot}} \rangle - d_U - \xi, \langle S^2_y \rangle + \langle S^2_z \rangle = \frac{3}{4} \langle n_{\text{tot}} \rangle - 3d_U + d_H - d_{\text{anti-H}} - 2\xi \).

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Nickel-Titanium double-perovskite:
A three-dimensional spin-1 Heisenberg antiferromagnet
Supplemental Material

M. Karolak, M. Edelmann and G. Sangiovanni
Institut für Theoretische Physik und Astrophysik,
Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

This Supplemental Material contains additional information on the Wannier functions for different numbers of bands in the projection, the full table of corresponding hopping amplitudes and the Hamiltonian used in the two band model.

WANNIER FUNCTIONS AND HOPPING INTEGRALS

Performing a projection of the two Ni $e_g$-bands on maximally-localized Wannier functions using the Wannier90 code package \cite{1} yields a representation of the effective orbitals contributing to the hopping in a two band direct exchange model. This results in two orbitals sitting on Ni that are warped from the atomic shape by hybridization with O and Ti, an $x^2-y^2$-like and a $3z^2-r^2$-like Wannier function whose isosurfaces are shown in Fig. 1a. Analogously, the projection of Ti $t_{2g}$-bands, all O $p$-bands and all Ni $d$-bands onto MLWFs yields Wannier functions the highly resemble those of atomic orbitals, as has been done for Fig. 1b. In Fig. 1b, one sees that the respective functions are strongly centered around the corresponding atoms (e.g. $p$ on O), indicating hybridization only takes place between the included bands.

From the projection onto MLWFs, the hopping integrals are obtained. A detailed list containing the hopping integrals for the relevant nearest-neighbor and next-nearest-neighbor hopping paths from the two-band model is presented in Tab.\n
![Isosurfaces of Wannier functions obtained by projection of (a) only the Ni $e_g$-bands and (b) all Ni $d$- and O $p$-bands. In (a), the upper left one is mainly of $x^2-y^2$ character and the lower right mainly of $3z^2-r^2$ character. The left and right coordinate system give the directions used in the paper and in Tab.\n]
TABLE I. Table of hopping parameters in meV between two Ni atoms within the crystal. Values are obtained via Wannier projection. First column indicates the position of the unit cell where the Ni hopped to sits, whereas the Ni hopped from sits in the cell at the origin (in the (i,j,k) coordinate system of Fig. 1). The number labeling in the second to fourth columns indicates the position and orbital of the two relevant Ni, where 1 and 3 stand for $3z^2-r^2$-like on atom 1 and 2, respectively, and 2 and 4 represent $x^2-y^2$-like on atom 1 and 2, respectively. Hopping is possible along 180° and 90° bonds.

MODEL HAMILTONIAN

The local interaction considered in the direct exchange model is of Kanamori type [2, 3], the fully SU(2)-symmetric interaction Hamiltonian reads

$$H_{\text{Kanamori}} = U \sum_m \hat{n}_m \sigma \hat{n}_m \sigma + \sum_{m \neq m', \sigma} [U' \hat{n}_m \sigma \hat{n}_{m', -\sigma} + (U' - J_H) \hat{n}_m \sigma \hat{n}_{m', \sigma}] + \frac{1}{2} J_H \sum_{m \neq m', \sigma} \left( \hat{c}_m \sigma \hat{c}_{m', -\sigma}^\dagger \hat{c}_{m', -\sigma}^\dagger \hat{c}_m \sigma - \hat{c}_m \sigma \hat{c}_{m', -\sigma} \hat{c}_{m', -\sigma}^\dagger \hat{c}_m \sigma \right),$$

(1)

with the number operator $\hat{n}_m \sigma = \hat{c}_m \sigma \hat{c}_m \sigma$, where $\hat{c}_m \sigma$ ($\hat{c}_m \sigma$) creates (annihilates) an electron with spin $\sigma$ in orbital $m$. Furthermore, we used $U' = U - 2J_H$, where $U$ represents the Hubbard repulsion and $J_H$ the Hund’s coupling.

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