Magnetoresistance in ultrafine powders of half-metallic perovskite manganites

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A model of conductance network is presented to study the magnetotransport properties of half-metallic nanopowders of perovskite manganites. The effects of superparamagnetism and high-order tunneling on the temperature dependence of magnetoresistance in such systems are examined and the results are consistent with experiments. Our model can also be applied to other ferromagnetic fine-granular systems and a good agreement with experiments is found as well.

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I. INTRODUCTION

Half-metallic ferromagnets were first proposed as a new class of materials by de Groot *et al.* in 1983.[1] The members of this class have simultaneously the property of an energy gap between valence and conduction band for one spin polarization and the property of continuous bands for another. As a consequence of such an asymmetric band character, the conduction electrons at the Fermi level are completely polarized, which is of considerable interest both for theoretical studies and for potential application.

Among the materials that have been proved half metallic in band-structure calculations or in experiments, doped manganites of the type $A_{1-x}B_xMnO_3$ (A=La, Nd; B=Ca, Ba, Sr) are undoubtedly one of the most studied for their remarkable magnetotransport properties. They are generally believed to be double-exchange ferromagnets and therefore, have a nearly 100% spin polarization below the Curie temperature T_c,[2] near which a surprisingly magnetoresistance (MR) is observed accompanied with a transition from a high-temperature paramagnetic insulator to a low-temperature ferromagnetic metal.[3,4] This so-called colossal MR (CMR) is restricted to a narrow range of temperatures around T_c and difficult to apply to electronic devices despite their large magnitude.

Another type of MR is also found in the polycrystalline samples of these materials at low temperatures. Hwang *et al.*[5] first described this phenomenon in detail by comparing polycrystalline ceramics with single crystal $(La_{0.67}Sr_{0.33})MnO_3$. The polycrystalline ceramics exhibited high resistivity values, which are far above that of the single crystal, and a sharp drop in the resistance at low fields. According to the experimental results, Hwang *et al.* ascribed the negative MR of the polycrystalline samples to spin-polarized tunneling through an insulating grain boundary separating metallic grains with high spin polarization. Actually, the double-exchange mechanism determines that, in most cases, electrons in these systems are able to move when the spins of the ions are parallel, and cannot move if they are unparallel.[6,7] So magnetic disorder in the interface region[8] will sharply increase the resistance of grain boundaries and form a tunneling barrier through which spin-polarized tunneling happens. The electron-tunneling probability depends on the relative orientation of magentization directions of neighboring grains, which can be substantially varied upon application of a magnetic field. Such a tunneling mechanism is especially obvious in powder compacts of these materials. One example is $(La_{0.7}Sr_{0.3})MnO_3$ powders prepared by Coey.[9] The intergranular resistance was estimated to be 1.6 MΩ, much larger than the quantum limit $R_Q=\hbar/2e^2 \simeq 12.9$ kΩ. This means metallic grains are truly isolated from one another (an insulating granular metal) and electron transport will be entirely by tunneling from grain to grain. Apart from doped manganites, granular systems of other half-metallic materials such as CrO_2 also exhibit similar large intergranular MR behavior and the spin-polarized tunneling through insulating grain boundaries is widely accepted as its origin.[10–12]

Very recently, attention has been drawn towards nanocrystalline perovskite manganites.[13–15] Particularly, the experimental work on nanoscale $La_{2/3}Ca_{1/3}MnO_3$ powders in Ref. 15 has shown distinct difference in magnetic and electrical properties between ultrafine powders and conventional bulk ceramics. With a grain size three orders smaller than the latter, the powder sample shows strong superparamagnetism above 95 K and behaves as an insulator between 5 K and 300 K. Most surprisingly, the magnetoresistance of powders can reach a maximum value of 100% at low temperatures, nearly double the usual value found in ceramics (50%–60%). However, the large MR drops rapidly after 100 K and vanishes gradually around 300 K.

The purpose of this paper is to explain these new properties found in the nanopowder systems. Based upon a model of tunneling magnetoresistance in insulating granular systems, we try to incorporate into MR calculations the effects of superparamagnetism and high-order tunneling through small grains with strong Coulomb blockade. It is found that these two factors are crucial to determine the temperature dependence of magnetoresistance in such a system. Our results can agree with the experiments qualitatively.

II. THEORY

A. Superparamagnetism

In the nanopowder system in Ref. 15, the high resistance across a wide range of temperatures (5 K–300 K) indicates that the tunneling conductance through insulating grain boundaries outweighs the intrinsic conductance of grains and dominates the whole transport process. So we can apply the conventional model of insulating ferromagntic granular systems[16–19] to the present case. This model treats a couple of grains separated by an insulating boundary as a small ferromagnetic junction. The tunneling process is controlled by the combination of spin-dependent tunneling and the charging energy E_c of grains, that is, the energy required to generate positively and negatively charged granules. Suppose tunneling can only occur between grains that are equal or nearly equal in size, the whole system can be represented by a conductance network in which the metal grains are connected by conductances G_{ij} in the form of

$$G_{ij}=G_{ij}^{T}\exp(-E_c/k_BT), \tag{1}$$

with G_{ij}^{T} referring to the tunneling mobility between the grains as[19]

$$G_{ij}^{T}\propto(1+P^2\cos\theta)e^{-2\kappa s}, \tag{2}$$

where

$$P=\frac{D_\uparrow-D_\downarrow}{D_\uparrow+D_\downarrow} \tag{3}$$

and

$$\kappa=\sqrt{2m_e\phi/\hbar^2}. \tag{4}$$

Here, θ is the angle between the magnetizations of two ferromagnetic grains, $D_\alpha(\alpha=\uparrow,\downarrow)$ is the density of states at the Fermi energy E_F for electrons with spin α, P is the spin polarization, and s, m_e, and ϕ are the thickness of the barrier, the effective mass of electrons, and the barrier height, respectively.

The distribution of E_c depends on that of the grain diameter D and of the barrier thickness s. Sheng[16] has pointed out that in order to ensure the homogeneity of the metallic grain concentration, the ratio D/s should have the same values for different regions in the system although both D and s may have a wide distribution. It follows that the product sE_c is invariant for the same composition of the sample, which can be written as[17]

$$\kappa sE_c=c, \tag{5}$$

where κ and c are both constant. Under this condition, the conductance of the system is given as[18]

$$\begin{aligned}G&=G_0\int\int ds\,d\theta f(s)g(\theta)\exp(-2\kappa s-E_c/k_BT)\\&=G_0(1+P^2m^2)\exp(-2\sqrt{2c/k_BT}),\end{aligned} \tag{6}$$

where m is the relative magnetization of the system, $f(s)$ and $g(\theta)$ are, respectively, the distribution functions of s and θ. Then the MR ratio, defined as $[1-G(0)/G(H)]$, is expressed as

$$MR=\frac{P^2m^2}{1+P^2m^2}. \tag{7}$$

For completely spin-polarized systems $(P=1)$, such a model produces a saturation MR with the value of 50%, which is in agreement with the experimental results of the bulk samples in Ref. 15 at low temperatures since that magnetoresistance is of the tunneling type described in the preceding section.

However, for real systems composed of ultrafine single-domain grains at a given temperature T, there always exists a critical size D_b. When the diameter D of a grain is smaller than D_b, the magnetic anisotropy energy barriers of the grain ($\sim KV$ with K as the anisotropic energy density and V as the grain volume) will be overcome by thermal energy ($\sim k_BT$) and superparamagnetic (SPM) relaxation occurs.[19] Otherwise, the grains will be blocked, which means they are prevented from reaching thermal equilibrium and behave as usual ferromagnetic (FM) grains. Then the tunneling conductances in these systems should be divided into two types: one is between FM grains, the other between SPM grains. Their expressions and corresponding fractions are determined by

$$G_1=G_0\int_{s_b}^{\infty}ds f(s)(1+P^2m_1^2)\exp(-2\kappa s-c/\kappa sk_BT),$$

$$f_1=\int_{D_b}^{\infty}f(D)dD, \tag{8}$$

$$G_2=G_0\int_{0}^{s_b}ds f(s)(1+P^2m_2^2)\exp(-2\kappa s-c/\kappa sk_BT),$$

$$f_2=\int_{0}^{D_b}f(D)dD, \tag{9}$$

where s_b is the value of barrier thickness corresponding to D_b since s/D is equal to a constant, which has been described above as one of the basic assumptions in the model of insulating granular systems proposed by Sheng *et al.*[16] $f(D)$ is the probability distribution of granular diameter D and m_1 (or m_2) refers to the reduced magnetization of FM (or SPM) grains. When applied to a magnetic field H, the magnetization of FM grains will rapidly reach its saturation value, $m_1=1$, while that of SPM will rise with increasing field as

$$m_2=\coth\left(\frac{\mu H}{k_BT}\right)-\frac{k_BT}{\mu H}. \tag{10}$$

At extremely low temperatures, since lots of grains are blocked, the tunneling between FM grains contributes most to the transport process and the MR ratio is close to the value obtained not considering the influence of superparamagnetism (MR=50% when P=1). With temperature rising, the number of SPM grains increases, causing the magnetoresistance decreasing quickly until most of the blocked grains are changed into superparamagnetic state. At a given temperature T and a magnetic field H, the effective conductance G_e of the system can be calculated in the scheme of the effective medium theory by[20]

$$f_1\frac{G_1-G_e}{G_1+(d-1)G_e}+f_2\frac{G_2-G_e}{G_2+(d-1)G_e}=0, \tag{11}$$

where d is the dimention of the system, and the MR ratio is determined by

$$MR=\frac{G_e(T,H)-G_e(T,0)}{G_e(T,0)}. \tag{12}$$

B. Cotunneling

Although the consideration of superparamagnetism can yield a temperature dependence of MR similar to the experimental results, the high MR at low temperature is still surprising since it has greatly surpassed the upper limit of theoretical expectation. We attribute this obvious enhancement of MR at low temperatures to tunneling between granules of different sizes, which has not been included in the above model. For ultrafine granular systems, there are many granules with the charging energy E_c higher than thermal energy k_BT and consequently have a low probability at which thermally activated charge carriers occupy them. These ''small'' granules separate among other charged ''large'' ones and cause higher-order processes of spin-dependent tunneling where the carrier is transferred through the array of ''small'' granules in the form of successive tunneling of single electrons, i.e., the cotunneling of electrons. The nth-order cotunneling conductance is given by[21]

$$G_c^n \propto \exp(-E_c'/k_BT-2\kappa s')(1+P^2m^2)^{(n+1)} \times\left\{\frac{(\pi T)^2}{(\delta E_c)^2+[\gamma(T)]^2}\right\}^n, \tag{13}$$

where δE_c is the Coulomb gap opened when an electron tunnels from the ''large'' granule to the ''small'' one, E_c' and s' are the charging energy and barrier thickness corresponding to the ''large'' granule, and $\gamma(T)$ is the decay rate of the intermediate states in the high-order process given by $\gamma(T)\simeq gT$ with g being a constant.

Taking into account cotunneling and superparamagnetism at the same time, we can get a more reasonable description of the system as a random conductance network. The properties of granules at a certain temperature are illustrated in Fig. 1, where D_b and D_c refer to the granular size corresponding to magnetic block temperature (T_B) and Coulomb energy (E_c), respectively. When the temperature is high, most granules will be unblocked both in magnetism and in charge carriers ($D_b>D_c$), so the ''small'' granules ($D<D_c$) are certainly superparamagnetic while the probabilities for the SPM and the FM ''large'' granules are, respectively, determined by

$$f_{SP}=\int_{D_c}^{D_b} f(D)dD,$$

$$f_F=\int_{D_b}^{\infty} f(D)dD. \tag{14}$$

The tunneling between these ''large'' granules may be direct or through some ''small'' granules. For simplicity, we only consider the first-order cotunneling, i.e., tunneling through only one ''small'' granule. By a rough estimation we obtain

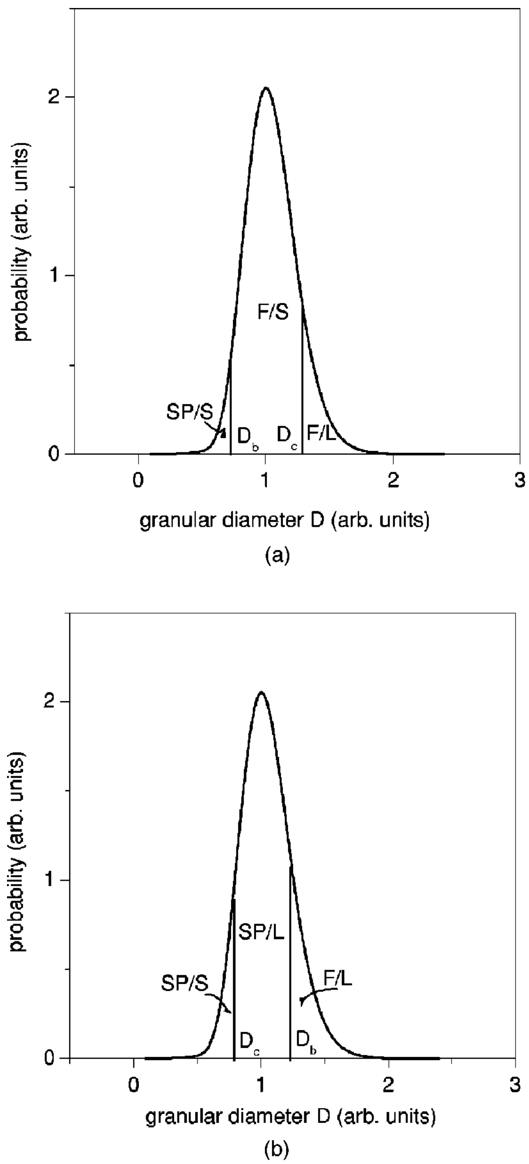

FIG. 1. Different grains at a certain temperature. L refers to large, S to small, F to ferromagnetic, and SP to superparamagnetic. (a) $D_b<D_c$ at low temperatures; (b) $D_b>D_c$ at high temperatures.

the ratio of direct tunneling paths to cotunneling paths as $p_d/p_c=(f_L-f_S)/f_S$ (when $f_S<f_L$). Here, f_S and f_L are the fractions of ''small'' and ''large'' granules,

$$f_S=\int_0^{D_c} f(D)dD,$$

$$f_L=\int_{D_c}^{\infty} f(D)dD. \tag{15}$$

When the number of ''small'' granules exceeds that of ''large'' ones, $f_S>f_L$, we suppose there are only cotunneling processes ($p_c=1, p_d=0$). Then it is obvious that the conductances in the network have four types [Fig. 2(b)],

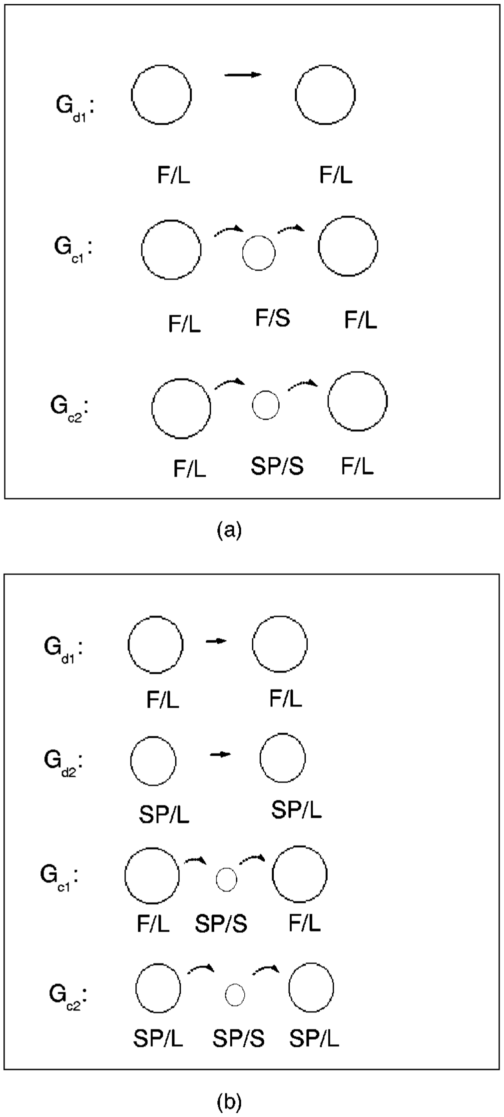

FIG. 2. Conduction paths at a certain temperature. (a) $D_b < D_c$ at low temperatures; (b) $D_b > D_c$ at high temperatures. Straight arrows refer to direct tunneling and curved arrows to cotunneling. Note that the grains in the figure have been far separated just in order to make the figure clear, while in real systems such as ceramics or powder compacts they are isolated from one another by a thin insulating layer.

$$G_{ij}=\begin{cases} G_{c1}, & FM-SPM-FM \\ G_{c2}, & SPM-SPM-SPM \\ G_{d1}, & FM-FM \\ G_{d2}, & SPM-SPM. \end{cases}$$

The detailed expressions of the conductances and their fractions are listed as follows:

$$G_{c1}=G_1\ \exp(-E_c'/k_BT-2\kappa s')\times(1+P^2m_1m_2)^2\frac{(\pi T)^2}{(\delta E_c)^2+[\gamma(T)]^2},$$

$$f_{c1}=f_Fp_c, \tag{16}$$

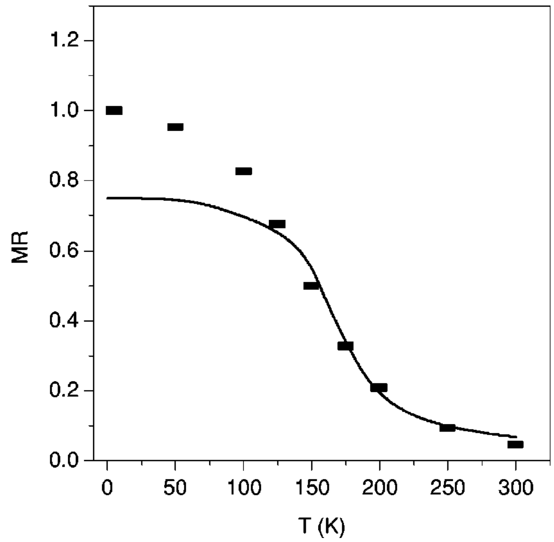

FIG. 3. The magnetoresistance curve (line) with temperature accompanied by experimental data from Ref. 15 (square). (D_0 $=18$ nm, $s=2.8$ nm, $\mu=61.79\mu_B$, $g=0.3$, $\delta=1.2$, $\kappa=0.1$ Å.)

$$G_{c2}=G_1\ \exp(-E_c'/k_BT-2\kappa s')\times(1+P^2m_2^2)^2\frac{(\pi T)^2}{(\delta E_c)^2+[\gamma(T)]^2},$$

$$f_{c2}=f_{SP}p_c, \tag{17}$$

$$G_{d1}=G_0\ \exp(-E_c'/k_BT-2\kappa s')(1+P^2m_1^2),$$

$$f_{d1}=f_Fp_d, \tag{18}$$

$$G_{d2}=G_0\ \exp(-E_c'/k_BT-2\kappa s')(1+P^2m_2^2),$$

$$f_{d2}=f_{SP}p_d. \tag{19}$$

Similarly, we get the types and fractions of link conductances when the temperature is low enough to make $D_b < D_c$ [see Figs. 1(a) and 2(a)]. Then the effective conductance and the magnetoresistance in the whole range of temperature can be obtained using effective medium theory to the network described above.

In order to calculate the magnetoresistance of the system, we select the log-normal size distribution used commonly in granular systems,[22]

$$f(D)\sim\exp\{-(\ln D-\ln D_0)^2/[2(\ln\delta)^2]\}. \tag{20}$$

Consequencely, the distribution of barrier thickness s is of the same type as that of D since their ratio is assumed to be constant,

$$f(s)\sim\exp\{-(\ln s-\ln s_0)^2/[2(\ln\delta)^2]\}. \tag{21}$$

The average charging energy E_c^0 is calculated approximately by[11,20]

$$E_c^0\simeq\frac{e^2}{4\pi\epsilon\epsilon_0D_0}. \tag{22}$$

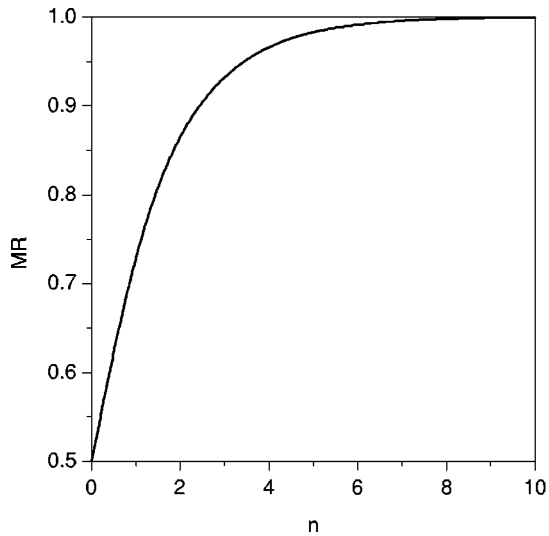

FIG. 4. Dependence of the magnetoresistance as a function of the cotunneling order n with $P=1$.

Here D_0 is the average grain diameter and the dielectiric constant is taken as $\epsilon=5$. The value of ϵ is smaller than that reported in ceramic samples of manganese perovskites ($\epsilon=10$).[23] However, considering the imperfection of powder boundaries and referring to the experiments on CrO_2 powders,[11] we believe this value is acceptable.

Another parameter difficult to determine is the ratio G_1/G_0. Fortunately, the calculated MR is not sensitive to its value between 0.01 and 1, which is the possible range according to Slonczewski's tunneling theory.[24] So we choose 0.1 as its value and give the temperature dependence of the magnetoresistance as shown in Fig. 3. Other parameters are taken either directly from the experiment in Ref. 15 or from data reported in work on similar systems.[21,22] Their values are listed in the caption of Fig. 3.

The calculated MR vs temperature curve in Fig. 3 can agree with the experiment, especially in the range from intermediate to high temperatures. At low temperatures, the MR value is smaller than that in the experiment, which comes from our neglect of cotunneling with higher order. Taking the limit case of $T\rightarrow 0$ as an example, at which nearly all granules have been both "small" and ferromagnetic, the main tunneling process tends to have an order much higher than one[21] and therefore, increases the magnetoresistance to a rather high value. Figure 4 gives a description of the rapid rising of MR with the increase of the cotunneling order n. It is shown that the value of MR can even reach nearly 100% when $n>6$. In order to test the validity of our model further, we apply it to the case with small charging energy, where the cotunneling order is expected to be low even at low temperatures.

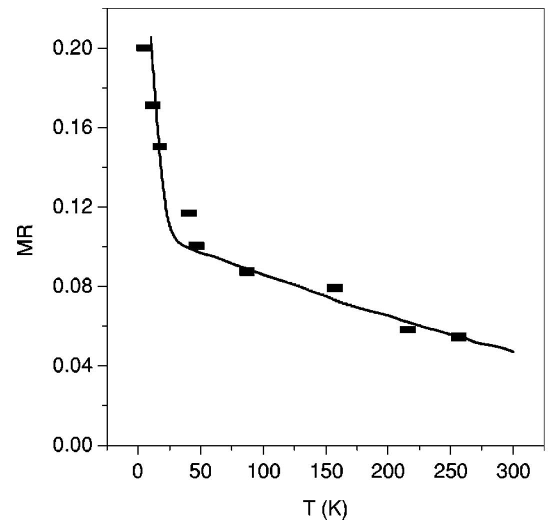

FIG. 5. The comparison between the calculated MR ($D_0=2$ nm, $s=3$ nm, $\kappa=0.1$ Å, $\mu=600\ \mu_B$, $g=0.3$, $\delta=1.2$, $P=0.35$, $E_c=18$ K) and the experimental results in Ref. 25.

Our results are compared with the experiments on $Fe\text{-}Al_2O_3$ granular films in Ref. 25. It can be seen from Fig. 5 that in that case ($E_c^0=18$ K) our model can get a temperature dependence of MR in good agreement with experiments.

III. CONCLUSIONS

In this paper, we present an extended model of insulating granular systems to explain the new magnetotransport properties found in recent experiments on nanopowders of perovskite manganites. It is shown that with the grain size decreasing into nanometers, both superparamagnetism and cotunneling will play an important role in determining the temperature dependence of the magnetoresistance. Particularly, cotunneling processes can enhance MR obviously at low temperatures while the existence of superparamagnetism tends to cause MR decaying with temperature increasing. Although these effects caused by nanostructure are especially obvious in half-metallic systems for their high spin polarization, our model can also be applied to other ferromagnetic granular systems in which tunneling processes are dominant.

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