

Absence of ferromagnetism in Co and Mn substituted polycrystalline ZnO

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We discuss the properties of semiconducting bulk ZnO when substituted with the magnetic transition metal ions Mn and Co, with substituent fraction ranging from $x=0.02$ to $x=0.15$. The magnetic properties were measured as a function of magnetic field and temperature and we find no evidence for magnetic ordering in these systems down to $T=2$ K. The magnetization can be fit by the sum of a Curie-Weiss term with a Weiss temperature of $\Theta \gg 100$ K and a Curie term. We attribute this behavior to contributions from both tM ions with tM nearest neighbors and from isolated spins. This particular functional form for the susceptibility is used to explain why no ordering is observed in tM substituted ZnO samples despite the large values of the Weiss temperature. We also discuss in detail the methods we used to minimize any impurity contributions to the magnetic signal.

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The ability to control spin as well as electric charge is a cornerstone of next generation spintronic devices. Attempts to inject spin-polarized current into nonmagnetic semiconductors using metallic ferromagnetic contacts have met with mixed success.^{1,2} Efficient spin injection between metallic and semiconducting systems appears to be possible only with an insulating tunnel junction separating the two.³⁻⁵ This complication could be removed by using a high temperature ferromagnetic semiconductor. Such a material would play a crucial role in the development of spintronic devices. Mn-substituted GaAs has been observed to have a ferromagnetic transition temperature of up to 172 K,⁶ but reports of transition temperatures above 300 K in Co-substituted TiO₂,⁷ among other systems may be attributed to sample inhomogeneities.⁸ Recent work on organic spin-valves⁹ have shown promising results, but in this paper we concentrate on semiconducting metal oxides.

One material which shows particular promise for yielding a suitable ferromagnetic semiconductor is ZnO. Zinc oxide is a wide band gap (3.3 eV) semiconductor, so a ferromagnetic version could also be used as a material for magneto-optical devices. ZnO substituted with 5% Mn was predicted to order magnetically above 300 K,¹⁰ and the ground state for ZnO substituted with other transition metal (tM) ions is predicted to be ferromagnetic.¹¹ Recently, there has been work in investigating the importance of p -type doping for producing ferromagnetic behavior in ZnO.¹² There have been a range of experiments done on Mn-substituted ZnO,¹³⁻¹⁵ with some investigation of ZnO substituted with other transition metals.¹⁵⁻¹⁸ Several measurements on Co- and Mn-substituted ZnO grown in thin films have found evidence for ferromagnetic behavior, but other measurements find no

magnetic transitions. It is thought that clustering of the magnetic ions into an impurity phase might be responsible for these features.¹⁹ One recent report finds evidence for room temperature ferromagnetism in bulk Mn:ZnO prepared using low temperature techniques.²⁰ Ferromagnetism has also been observed in Co:ZnO semiconducting quantum dots,²¹ but the magnetic properties of nanoparticles can differ from bulk behavior.²²

In light of these discrepancies in earlier measurements on the magnetic properties of tM substituted ZnO, we have undertaken a study of bulk Mn _{x} Zn _{$1-x$} O and Co _{x} Zn _{$1-x$} O samples which we hope will resolve some of the ambiguities surrounding reports of ferromagnetism in these systems. We investigate bulk samples to minimize the contribution of extrinsic effects from surface impurities. Furthermore, by exploring samples with a range of tM fractions prepared using the same technique, we can investigate systematic trends in these compounds. Finally, our measurements are structured to search for and eliminate any possible contributions from the magnetic impurities which have plagued earlier studies. Specifically, investigating the differential high field susceptibility, as described below, eliminates any potential contributions to the signal from magnetic impurities not detected by our characterization techniques. This is necessary because magnetic measurements are a much more sensitive probe of ferromagnetic impurities than other characterization techniques.

In order to investigate the magnetic properties of ZnO: tM , we examined bulk samples of Mn _{x} Zn _{$1-x$} O and Co _{x} Zn _{$1-x$} O with x ranging from 0.02 to 0.15. It has been found previously that substitution above these levels leads to the development of a spinel phase related to Co₃O₄ in

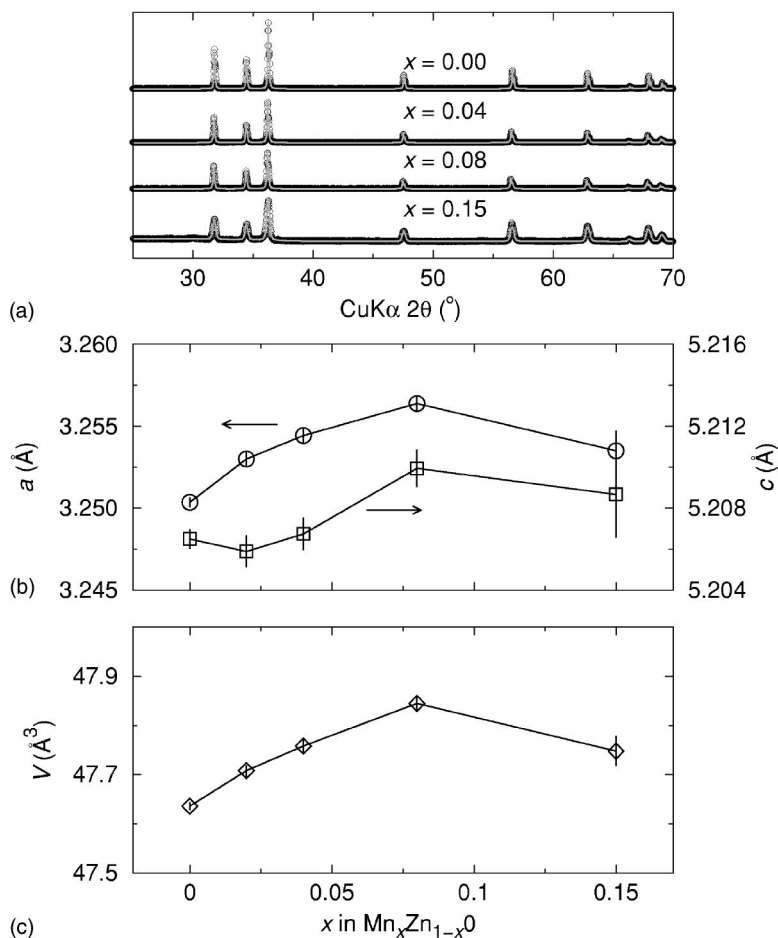


FIG. 1. (a) X-ray diffraction patterns (experimental data as circles and Rietveld simulations as lines) of $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ for different x values as indicated in figure. (b) Evolution of the a and c cell parameters with increasing x in $\text{Mn}_x\text{Zn}_{1-x}\text{O}$. (c) Evolution of the cell volume with x . In (b) and (c) 3σ error bars are indicated.

$\text{Co}_x\text{Zn}_{1-x}\text{O}$ (Ref. 16) so we confine our experiments to smaller values of x . To obtain bulk $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ and $\text{Co}_x\text{Zn}_{1-x}\text{O}$ samples, a single-source crystalline precursor is useful in order to ensure random atomic scale mixing of Zn^{2+} and $\text{Mn}^{2+}/\text{Co}^{2+}$ ions on lattice sites prior to decomposition. In addition, decomposition of oxalate precursors allows the removal of carbon as CO and CO_2 , leaving a phase-pure oxide product. Preparation and evidence for the formation of homogeneous solid solutions in bulk $\text{Co}_x\text{Zn}_{1-x}\text{O}$ has been previously described in detail.¹⁶ In a similar manner, $\text{Zn}_{1-x}\text{Mn}_x(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ oxalate precursors were made with $x=0.02$ through $x=0.15$. These precursors were decomposed in air at 1373 K for 15 minutes (with the sample placed and pulled out of the furnace at temperature). We performed elemental x-ray analysis on the Co substituted samples, confirming the Co fractions.

Powder x-ray diffraction (XRD) patterns were recorded on a Scintag X2 diffractometer in the Bragg-Brentano configuration using $\text{CuK}\alpha$ radiation. Data were collected using a step scan of 0.015° in 2θ and subject to Rietveld profile analysis using the XND Rietveld code.²³ Powder x-ray diffraction data are shown in Fig. 1 for the compositions $x=0.00, 0.04, 0.08$, and 0.15 for $\text{Mn}_x\text{Zn}_{1-x}\text{O}$. Points are data and the solid lines are Rietveld fits. None of the samples in this compositional range showed any evidence for impurity phases. As the amount of Mn increases, the x-ray peak widths increase suggesting that crystalline correlation is decreased. This is consistent with the low natural solubility of

Mn^{2+} in the ZnO lattice. Evolution of lattice parameters, as obtained from the Rietveld refinement, with x is shown for the $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ in panel (b) and the evolution of the cell volume in panel (c). The cell parameter evolution is not simple; the a cell parameter increases linearly with x only from $x=0$ to $x=0.08$, which seems to be a limiting composition. The c parameter first decreases slightly, and then increases. Again, $x=0.08$ seems to be a limiting composition. Substitution of the smaller Zn^{2+} ion (radius= 0.60 \AA) by the larger Mn^{2+} ion (radius= 0.66 \AA) should result in an increase in the unit cell volume. This increase is once again, systematic until $x=0.08$ as seen in Fig. 1. Slight differences are seen in our results from those recently published by Kolesnik, Dabrowski, and Mais,¹⁸ who report, for $x=0, 0.05, 0.10, 0.15$, and 0.20 , that a, c , and V increase smoothly with x but the $x=0.15$ sample is not single phase. Because of this, we restrict our magnetic measurements on $\text{Mn}_x\text{Zn}_{1-x}\text{O}$, to samples with x below 0.10 .

Magnetic measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). For each measurement, we used roughly 30 mg of sample which gave a signal over three orders of magnitude larger than the magnetic background of the sample holder. We measured both the magnetization as a function of field at fixed temperature, and the temperature dependence of the susceptibility. In order to accurately determine the intrinsic magnetization of the sample as a function of temperature, we measured the differ-

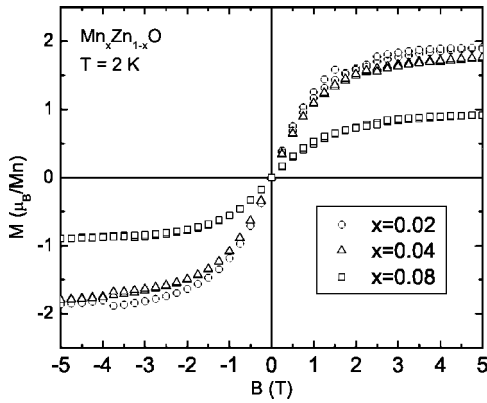


FIG. 2. Magnetic moment per Mn^{2+} as a function of external field at $T=2$ K. The magnetization of $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ is plotted for four values of x ranging from $x=0.02$ to $x=0.08$.

ential susceptibility by subtracting the magnetic moment at $B=1$ T from the moment measured at $B=2$ T at each temperature. The background susceptibility of ZnO was measured separately and subtracted. This background contribution was roughly 10% of the total susceptibility at high temperatures.

Because impurity contributions have previously been misidentified as intrinsic effects,¹⁹ it is vital to ensure that we are unable to detect any impurities in the sample, and also that any impurity contribution to the magnetization is removed. We know from XRD that any crystalline impurity fraction must be below the 1% level. In addition, low field susceptibility measurements as function of magnetic field at fixed temperature show no deviation from strictly linear behavior. We take this as evidence for both the lack of impurities, and that the $t\text{M}$ ions are fully substituting into the lattice. As a final check for impurities, we measured specific heat of the $x=0.15$ sample (which would be expected to have the largest impurity contributions), since this is a bulk probe of magnetic order, even down to very small impurity fractions. The absence of any signal in specific heat arising from long range order in magnetic impurities is consistent with the magnetic measurements and suggests that we are probing the intrinsic properties of $t\text{M}$ -substituted ZnO. Additionally, by measuring the differential susceptibility as described above, we can be certain that any spurious contribution to the signal from ferromagnetic impurity clusters not identified by the characterizations discussed above will be eliminated.

We plot the magnetization as a function of magnetic field at $T=2$ K for $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ for different values of x in Fig. 2. These magnetization data suggest that there are contributions to the magnetic signal from both free spins and spins associated with antiferromagnetic clusters. The suppression of the net magnetic moment seen as x is increased is opposite to expectations based on free Mn impurity spins. Since $x=0.08$ is within a factor of 2 of the three-dimensional (3D) percolation threshold on the ZnO lattice, one would expect to see effects from clustering. This would lead to a reduction of the measured moment if the pure Mn end-member were antiferromagnetic. We observe that the moment is large for the lowest concentrations ($x=0.02$ and $x=0.04$), but becomes smaller as the substituent concentration increases. The mo-

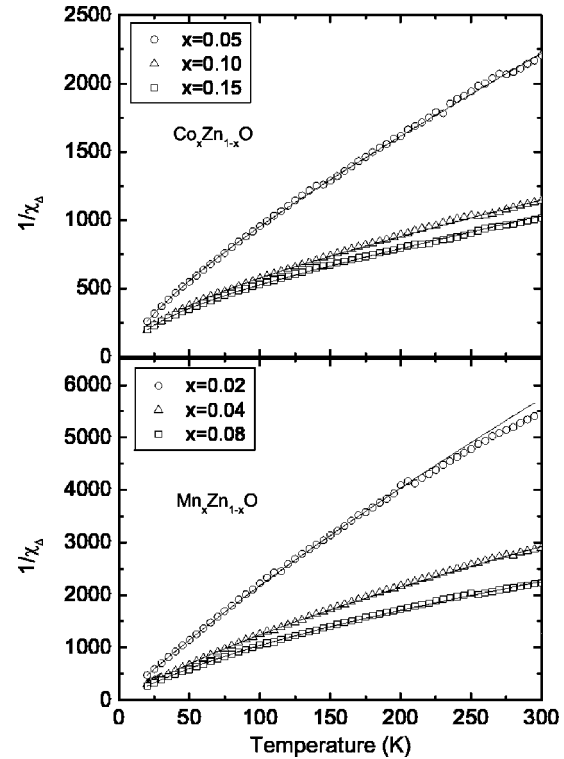


FIG. 3. Inverse susceptibility for $\text{Co}_x\text{Zn}_{1-x}\text{O}$ (upper panel) and $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ (lower panel) as a function of temperature. The susceptibility was determined by looking at the difference in magnetization between $B=2$ T and $B=1$ T. The solid lines show fits to the function defined in Eq. (1).

ment plotted in Fig. 2 arises predominantly from free spins in the system. With increasing x , the fraction of Mn ions belonging to antiferromagnetic clusters which do not contribute to the magnetic signal increases, which reduces the net magnetization. This behavior is very similar to that previously observed in $\text{Co}_x\text{Zn}_{1-x}\text{O}$.¹⁶ Furthermore, the $M(B)$ curves shown in Fig. 2 show no evidence for magnetic hysteresis even at $T=2$ K; there is no ferromagnetic transition in $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ above this temperature. This observation is in contrast to a report on room temperature ferromagnetism in $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ at $x=0.02$,²⁰ which found evidence for a very small ferromagnetic moment in samples prepared under relatively low temperature conditions. The origin for this discrepancy is unclear, although there are suggestions that these earlier measurements were sensitive to unreacted manganese oxides.²⁴

The temperature dependence of the magnetizations of $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ and $\text{Co}_x\text{Zn}_{1-x}\text{O}$ are plotted in Fig. 3 as inverse susceptibility versus temperature. These plots show characteristic behavior observed in other $t\text{M}$ -substituted ZnO samples, namely a high temperature regime that appears to be close to linear, followed by significant curvature at lower temperatures. Furthermore, there is a systematic variation in the high temperature magnetization with substitution fraction. The samples with the smallest values of x show larger values of $1/\chi$, and the inverse susceptibility decreases monotonically with increasing x as has been observed previously.

In order to analyze such data, it is typical to make a linear

fit of the high temperature inverse susceptibility which models Curie-Weiss behavior. This approach is motivated by prior work on dilute magnetic semiconductors which predicts that the high temperature magnetization should follow a modified Curie-Weiss law, where the Curie constant and Curie-Weiss temperature are scaled by the substituent concentration x .²⁵ While this model appears to accurately predict the properties of Se and Te based semiconductors even at lower temperatures where there are significant deviations from Curie-Weiss behavior,^{25,26} we find discrepancies when attempting to apply this formalism to $\text{Co}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mn}_x\text{Zn}_{1-x}\text{O}$, particularly in fitting the low temperature susceptibility. Furthermore, applying this analysis to $\text{ZnO}:\text{tM}$ samples gives a wide range of very large values for the Weiss temperature [from $\Theta_0=960$ K to $\Theta_0=1900$ K for $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ (Ref. 13)] despite the absence of any magnetic order above $T=20$ K.

To interpret our results, we propose a heuristic model based on two sets of substituent tM spins, motivated by Fig. 2 and the subsequent discussion. There is perhaps a hint of such behavior observed in NMR studies on $\text{Cd}_{1-x}\text{Co}_x\text{S}$ and $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ where it was observed that the splitting of the ^{113}Cd spectra can be explained by appealing to different relative connections to the paramagnetic substituents.²⁷ We assume that one of these subsets of spins (those tM ions with no tM nearest neighbors) is completely free, so the susceptibility follows a simple Curie behavior. The second set of spins (those tM ions with at least one tM nearest neighbor) is however affected by mean field interactions with a susceptibility which is expressed as a Curie-Weiss function. We find that separating the tM ions into two noninteracting subsets, namely isolated spins and clustered spins, gives an excellent fit to the susceptibility over the entire temperature range. We also allow for the possibility that the Curie constants will be different for the two terms. In particular, we assume

$$\chi = \frac{C_1}{T} + \frac{C_2}{T + \Theta} \quad (1)$$

in order to fit the magnetization data for $\text{Co}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mn}_x\text{Zn}_{1-x}\text{O}$. The solid lines in Fig. 3 show the fits to Eq. (1), which accurately capture both the high temperature behavior and the increasing curvature in χ^{-1} at lower temperatures.

An important observation is that only a subset of the spins are affected by magnetic interactions. For Mn-substituted ZnO, the value of Θ lies between roughly +190 K and +360 K for all samples measured. This suggests that the spins belonging to tM clusters are affected by antiferromagnetic mean field interactions, consistent with the $M(B)$ behavior plotted in Fig. 2. Very similar properties are observed for $\text{Co}_x\text{Zn}_{1-x}\text{O}$, but the value of Θ ranges from +160 K ($x=0.05$) to +250 K ($x=0.15$).

Since C_1 and C_2 play the role of Curie constants, we can use these fit values to extract the effective moment for the tM spins. Since we assume C_1 arises from tM ions with zero tM nearest neighbor (NN) ions, we need to scale C_1 by the fraction of tM meeting this condition. We computed the relative fraction of tM ions with zero tM nearest neighbors as a function of x by assuming random substitution of tM on the Zn

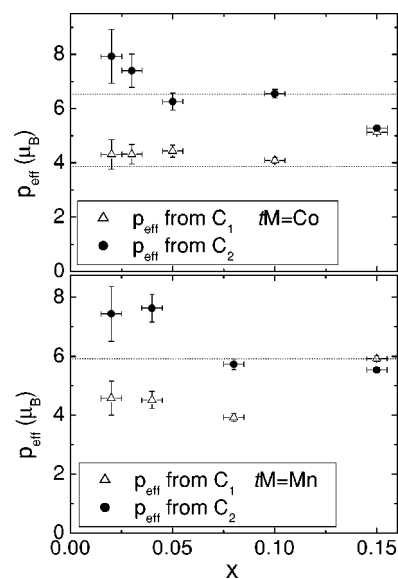


FIG. 4. Effective moments for the isolated (open symbols) and clustered (filled symbols) Co^{2+} (upper panel) and Mn^{2+} spins (lower panel). The dotted lines show the expected values of the spin-only and full-spin moments for the Co ions and the spin-only moment appropriate for Mn ions. Note that while we believe the $x=0.15$ ZnO:Mn sample is not single phase, we are able to extract a very accurate value for the effective moment. The error bars reflect the uncertainty in determining x (± 0.005).

site. The effective moment of the isolated tM spins was determined from the value of C_1 scaled by the fraction of tM ions with zero tM nearest neighbors. In a similar manner we computed the effective moment of the clustered spins from the value of C_2 scaled by the fraction of clustered spins. The results of these calculations are shown in Fig. 4 for both $\text{tM}=\text{Co}$ and $\text{tM}=\text{Mn}$. The error bars reflect the uncertainty in determining the value of x (which is only accurate to ± 0.005). These plots also show the expected values for the effective moments. For the Mn^{2+} spins the moment should be $5.92\mu_B$, while for Co^{2+} it can range between $3.87\mu_B$ (spin only value) and $6.54\mu_B$, with values around $4.8\mu_B$ being typically measured.²⁸ We find that the average effective moment (taking the intermediate point between the isolated and clustered spin contributions) for both the Co^{2+} and Mn^{2+} spins are reasonably close to the expected values. Our analysis suggests that for small x the effective moment for the clustered spins is larger than the effective moment for the isolated spins. At present, we do not understand the reason for this observation.

This analysis of the magnetic properties of tM substituted ZnO reveals several features. By investigating a series of compounds with different tM fractions, we find clear evidence for a systematic clustering of spins as the proportion of magnetic ions is increased. Additionally, we find that the dominant spin-spin interactions are antiferromagnetic, in agreement with other published results.¹³ Finally, we offer a simple explanation as to why these strong antiferromagnetic interactions do not lead to long range spin ordering. If we assume that the spins are localized and have no itinerant character, the lack of magnetic order arises from geometrical

considerations. The 3D site percolation threshold for an FCC lattice (having the same numbers of nearest neighbors as the wurtzite lattice) is 19.5%,²⁹ which is significantly higher than the maximum tM substitution of 10% for these samples. Since the concentration of magnetic ions is well below the percolation threshold, we would not expect to find magnetic order in these systems, at least at temperatures commensurate with the interaction strengths (few hundred K).

In summary, our measurements on a series of $\text{Co}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ samples with x ranging from 0.01 to 0.15 show no evidence for a ferromagnetic transition in these systems above $T=2$ K. At low temperatures, the characteristic dependence of the magnetic moment in $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ on B suggests that the dominant interactions are antiferromagnetic, as observed previously in $\text{Co}_x\text{Zn}_{1-x}\text{O}$ samples prepared under similar conditions.¹⁶ The important finding is that susceptibility data in both systems are fitted very well over a large temperature range by the sum of two Curie-Weiss functions. The fits yield a high temperature antiferromagnetic interaction ($\Theta \gg 100$ K) which we associate with NN interactions among the magnetic clusters, while the susceptibility of the spins with no magnetic nearest neighbors can be fitted very well by a simple Curie function. We hope to verify the

presence of two distinct spin populations in tM substituted ZnO using techniques such as electron paramagnetic resonance or Mössbauer spectroscopy.

Experimentally, we find that the dominant interactions in these systems are antiferromagnetic consistent with other recent measurements on these compounds.^{13,16} It is becoming increasingly difficult to envision a scenario whereby substitution of ZnO with either Mn or Co would produce a ferromagnetic ground state, at least at temperatures above a few K. This is consistent with recent work highlighting the importance of hole substitution in $\text{Co}_x\text{Zn}_{1-x}\text{O}$ or $\text{Mn}_x\text{Zn}_{1-x}\text{O}$ to obtain carrier-mediated ferromagnetism.¹²

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