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2009 J. Phys.: Condens. Matter 21 075801

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Anomalous x-ray diffraction peak broadening and lattice strains in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ dilute magnetic semiconductors

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Received 25 October 2008, in final form 25 December 2008

Published 23 January 2009

Online at stacks.iop.org/JPhysCM/21/075801

Abstract

Nanocrystalline powders of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ synthesized by the coprecipitation technique show anomalous anisotropic broadening for $x > 0.05$. This peak broadening is shown to be not only due to a reduction in the particle size but also due to a significant strain contribution, as confirmed by Williamson–Hall analysis. The presence of grouped Co^{2+} ions, revealing the presence of clusters of high spin Co^{2+} with antiferromagnetically coupled spins, as indicated by magnetization studies, seems to be responsible for the strain.

1. Introduction

Wide bandgap semiconductors doped with magnetic impurities, such as (Ga, Mn)N, (Ga, Cr)N and (Zn, Co)O, are theoretically predicted to be the most promising candidates for achieving high Curie transition temperatures (T_c) [1]. These are commonly known as dilute magnetic semiconductors (DMSs) with potential applications in spintronic devices [2–4]. A recent review article summarizes the magnetic behaviour in transition metal doped ZnO thin film and their possible applications in spintronics [5]. Theoretical studies reveal that the mean-field treatment of wide bandgap DMS systems overestimates T_c at low dopant concentrations [6–8]. Notwithstanding the predictions of these non-mean-field treatments, high T_c above room temperature (RT) has been reported experimentally for lower dopant concentrations [9]. A possible theoretical explanation for such high T_c in DMS materials has been advanced by Sato *et al* [10] in terms of the formation of percolative clusters of magnetic ions by a

spinodal decomposition process in analogy with the spinodal decomposition observed in alloys. This theory successfully explains the high T_c for magnetic impurity concentrations higher than 20%. For lower dopant concentrations, the magnetic clusters are well below the percolation threshold limit precluding a ferromagnetic transition, but may exhibit blocking effects due to the superparamagnetic nature of the isolated clusters [10].

The present work was undertaken to capture the structural and microstructural signatures of spinodal decomposition in Co doped ZnO nanoparticles prepared by the coprecipitation technique. It is shown that, for more than 5% Co concentrations, some of the wurtzite peaks exhibit anomalously large broadening. Williamson–Hall plots for such compositions reveal that the anomalous broadening is not entirely due to reduced coherently scattering domain size, but there is a significant strain contribution too. We attribute this strain to clustering of high spin state Co^{2+} ions, possibly due to the spinodal decomposition process predicted theoretically by Sato *et al* [10]. Our magnetization measurements provide additional support for such a clustering of Co^{2+} ions.

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2. Experimental details

$\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x = 0, 0.01, 0.025, 0.05, 0.1, 0.15, 0.2, 0.25$) powders were synthesized by the coprecipitation route. The starting materials were zinc and cobalt nitrates. NaOH was used as the precipitating agent. Equimolar solutions of the above compounds and a 4 M solution of NaOH were used for coprecipitation. The precipitated mixture was calcined in air at 150°C for 24 h. The dried powders were characterized by (i) x-ray diffraction (XRD) using an 18 kW rotating anode (Cu $K\alpha$) based Rigaku powder diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam, (ii) transmission electron microscopy (TEM model Tecnai 20 G2) and (iii) x-ray photoemission spectroscopy using an Mg and Al twin anode x-ray gun. Magnetic measurements were carried out using a physical property measurement system (PPMS) from Quantum Design.

3. Results and discussion

Figure 1(a) depicts the x-ray powder diffraction patterns of the as-synthesized samples with and without Co doping. For pure ZnO, all the peaks correspond to the wurtzite phase (space group $P6_3mc$), as expected. Co-doping does not lead to the appearance or disappearance of any of the wurtzite peaks, confirming that the structure of the doped ZnO remains wurtzite. We find that the limit of solid solubility of Co in ZnO is not exceeded for $x = 0.20$, as revealed by the appearance of a peak at $2\theta = 25^\circ, 44^\circ$ and 51° , marked with an asterisk in figure 1(a). These peaks could be due to some unidentified phase(s). Most of the existing reports indicate that Co has a limited solubility in ZnO up to ~ 15 at.% in polycrystalline samples [11]. Our results are in broad agreement with the findings of previous workers [11–15]. Co substitution gradually increases the unit cell volume (V) with increasing x up to $x \leq 0.05$, as can be seen from figure 1(b), which depicts the variation of V with x . For $x > 0.05$, the unit cell volume decreases with increase in x . It is interesting to note that, though all peaks broaden, the width of several reflections (e.g. 102, 110, 103 and 200) shows an anomalous increase for Co concentrations higher than $x = 0.05$. This is shown more clearly for the 2θ range 45° – 65° in figure 1(c). The fact that the onset of anomalous broadening and the decrease in the unit cell volume both occur for $x > 0.05$ suggests a close link between the two, and we proceed to discuss the possible origin of both.

In order to understand the origin of the anomalous broadening for compositions $x > 0.05$, we carried out Williamson–Hall (W–H) analysis [16] of the FWHM (β) of various Bragg peaks in figure 1, after removing the $K\alpha_2$ contribution and the instrumental broadening effects. In this analysis, one plots $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$, where θ is the Bragg angle. For pure particle size broadening this plot is expected to be a horizontal line parallel to the $\sin \theta$ axis, whereas in the presence of strain, it has a non-zero slope. The W–H plots for $x = 0, 0.05$ and 0.10 are shown in figure 2. It is evident from this figure that the slope of the linear fit remains almost the same for $x = 0$ and 0.05 , but increases

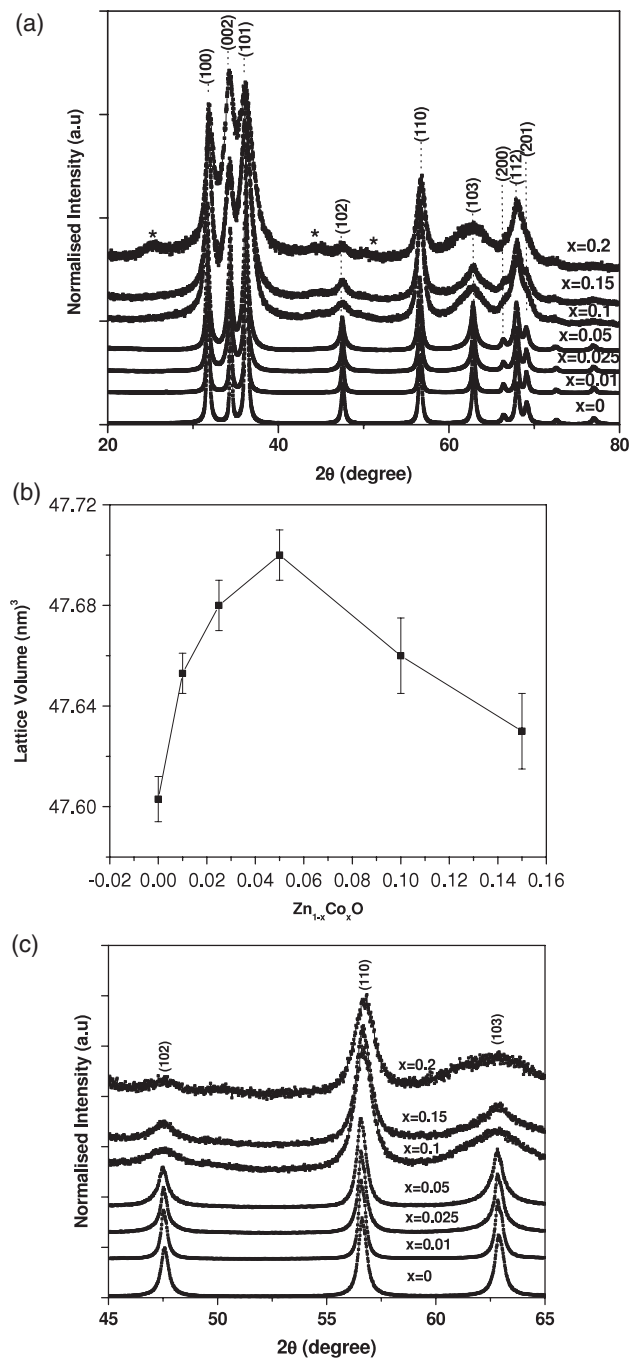


Figure 1. (a) X-ray diffraction spectra of pure ZnO and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ (*' denotes the impurity phase). (b) The lattice volume as a function of x in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ and (c) the anisotropic peak broadening of (102), (110) and (103) reflections.

quite significantly on increasing x from 0.05 to 0.10. The particle size obtained from the intercept of the straight line fits in figure 2 comes out to be ~ 35 nm for $x = 0$ and 0.05 and ~ 15 nm for $x = 0.10$. The strain and particle size calculated from the W–H plot are given in the inset of figure 2. The W–H analysis shows that the particle size decreases by about 50% on increasing x from 0.05 to 0.10, whereas strain increases by an order of magnitude (see the values given in the inset of figure 2). This implies that the anomalous broadening of some

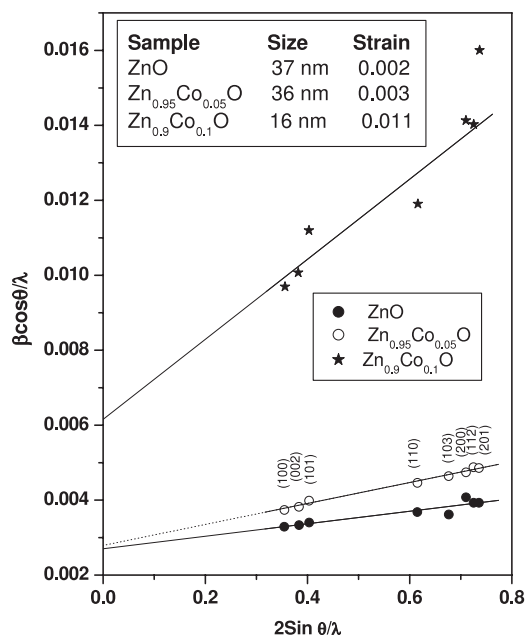


Figure 2. Williamson–Hall plot for Zn_{1-x}Co_xO ($x = 0, 0.05, 0.1$). The inset shows the size and strain calculated from the intercept and the slope of the linear fit, respectively.

of the peaks in figure 1(a) is not only due to size, but also due to a significant increase in strain. Unlike the data points for $x = 0$ and 0.05 in figure 2 which all lie on one straight line, the data points for $x = 0.10$ do not fall on the same straight line. This suggests that the strain is anisotropic for $x = 0.1$. This is also the reason why some of the peaks are broadened more than others. The decrease in the particle size on increasing x from 0.05 to 0.10 was also confirmed in TEM studies (see figure 3). We believe that the order of magnitude increase in strain could be due to the clustering of Co²⁺ ions and/or mixed occupancy at tetrahedral and octahedral coordinated sites as well. The size difference of Co²⁺ in an octahedral environment and Zn²⁺ ions in a tetrahedral environment may therefore be responsible for the development of strain in the matrix. Since Co can exist in different valence states, whose ionic radii are

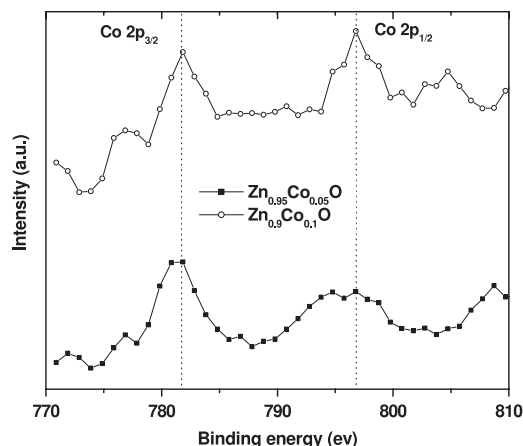


Figure 4. X-ray photoelectron spectra of Co 2P level for Zn_{0.95}Co_{0.05}O and Zn_{0.9}Co_{0.1}O samples.

also different, such a change of valence may contribute to the strain as well. In order to settle this issue, we carried out x-ray photoelectron spectroscopic measurements for $x = 0.05$ and 0.1 compositions. The binding energies of 780.55 and 796.0 eV respectively, for Co $2p_{3/2}$ and Co $2p_{1/2}$ states, clearly rule out the presence of Co³⁺ ions in these samples (see figure 4 for the x-ray photoelectron spectra). Having settled that the valence state of Co remains 2+ for $x = 0.05$ and 0.10 , the next issue to be settled is whether the broadening of the x-ray peaks could be due to the strain produced by the clustering of these ions. This was settled using magnetization measurements.

Magnetization (M) as a function temperature (T) at a fixed field of 0.5 kOe were measured for $x = 0.05$ and 0.1 and the results are shown in figure 5. The temperature dependence of magnetization for both the samples shows identical behaviour under zero field cooling and field cooling, which eliminates the possibility of superparamagnetic behaviour within the measurement temperature range of 2 – 150 K. We measured the M – H curve with increasing and decreasing applied magnetic fields in the positive quadrant of the M – H loop for $x = 0.05$ and 0.10 . The results are shown in figure 6(a). We did not see any hysteresis.

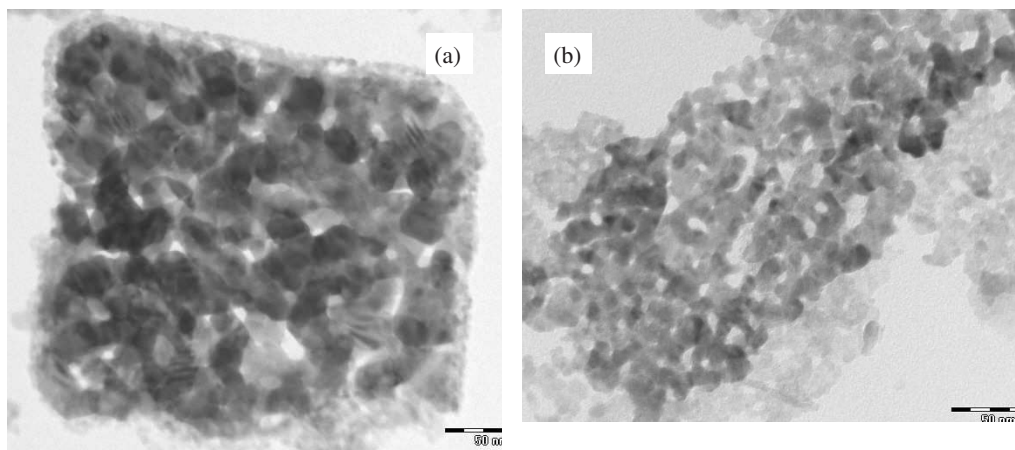


Figure 3. Typical transmission electron micrographs of (a) Zn_{0.95}Co_{0.05}O and (b) Zn_{0.9}Co_{0.1}O.

Table 1. Results after fitting the magnetic susceptibility versus temperature curves to the function given in equation (1) in the text for Co = 0.05 and 0.10.

Samples	C_1 (K)	C_2 (K)	$k \times 10^{-5}$	θ (K)	μ_{eff} from C_1 (μ_B)	μ_{eff} from C_2 (μ_B)
$\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$	0.01347	0.0279	-3.5	25.0	3.225	3.64
$\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$	0.0161	0.073	-9.5	91.0	3.225	6.87

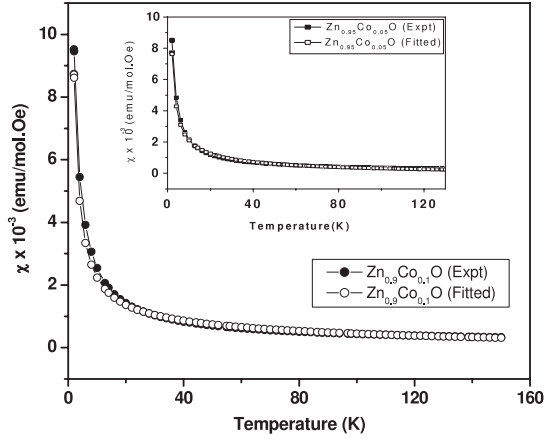


Figure 5. Magnetic susceptibility (χ) as a function of temperature for the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ sample and fitted curve with function defined in equation (1). The inset shows the experimental data and fitted curve for $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$.

The $M-H$ curve obtained by increasing field is retraced while decreasing the field. This clearly indicates the absence of ferromagnetism. The $M-H$ plot shown in figure 6(a) reveals reduction of measured moments on increasing the Co^{2+} content from $x = 0.05$ to 0.10. This has also been reported by earlier workers [17] and has been attributed to the presence of Co^{2+} clusters with antiferromagnetically coupled moments. The fraction of such clustered Co^{2+} ions increases with Co^{2+} concentration (x), leading to a reduction of net magnetization. The susceptibility/magnetization versus temperature plots (figure 5) seem to indicate characteristic paramagnetic behaviour, with a linear high temperature regime in agreement with previous workers [12, 17]. Fitting the linear regime with a Brillouin function, however, we found significant deviation between the experimental and theoretical curves at low temperatures, which suggests that it is not a perfect paramagnetic material. This type of deviation has also been reported by others [17, 18]. The extrapolation of the high temperature regime in the Curie-Weiss plot (figure 6(b)) gives negative Curie-Weiss temperature, suggesting antiferromagnetic correlations at low temperatures. However, the transition from paramagnetic to antiferromagnetic could not be seen even up to 2 K for $x \leq 0.10$. The paramagnetic nature of the susceptibility/magnetization data in the high temperature regime and deviation from the paramagnetic behaviour in the low temperature regime have motivated previous workers [17, 18] to fit the data with a combination of three functions corresponding to the contributions from (i) free cobalt spins giving rise to paramagnetic behaviour, C_1/T ,

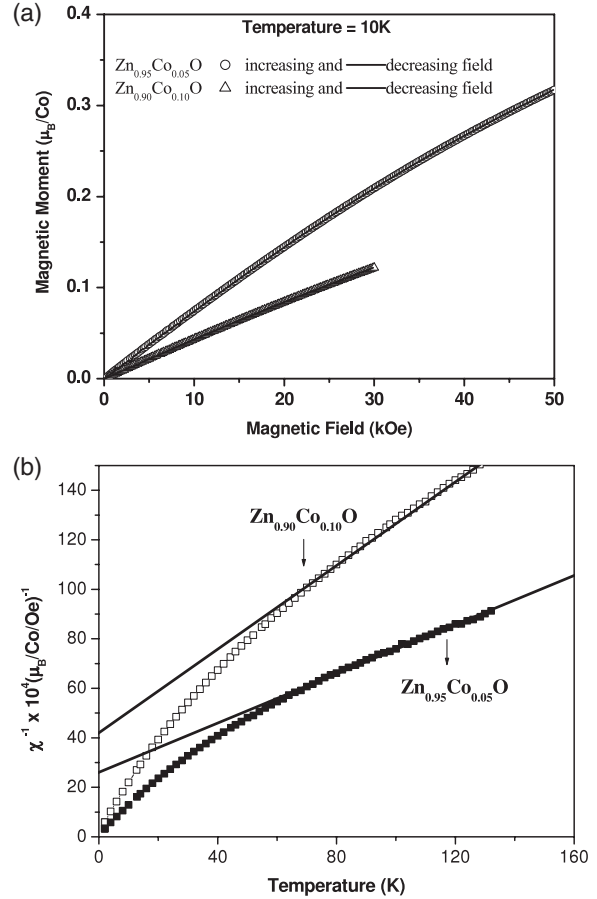


Figure 6. (a) Magnetization versus external magnetic field for both $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ and $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$. (b) Inverse of magnetic susceptibility as a function of temperature, which is extrapolated to zero in the temperature axis.

(ii) antiferromagnetically correlated Co spins with one or more Co^{2+} ions as nearest neighbours, $C_2/(T + \theta)$ and (iii) the diamagnetic ZnO matrix, k :

$$\chi = C_1/T + C_2/(T + \theta) + k. \quad (1)$$

The fit obtained using the above expression is quite satisfactory, as can be seen from figure 5. The fitted parameters are given in table 1. The background diamagnetic contribution, k , is found to lie in between -3.5×10^{-5} and -9.5×10^{-5} , which is comparable to the diamagnetic constant (-1×10^{-4}) of the ZnO matrix [19]. The effective magnetic moment as calculated from C_1 is $3.225 \mu_B$, while those from C_2 are 3.64 and $6.87 \mu_B$ for $x = 0.05$ and 0.10, respectively. The magnetic moment for free spins derived from C_1 is lower than the value for divalent Co with high spin configuration ($3.87 \mu_B$). If one

assumes completely random distribution of Co^{2+} ions, μ_{eff} values for isolated and grouped Co spins are reported to be $3.10 \mu_{\text{B}}$ and $5.85 \mu_{\text{B}}$ for $x = 0.05$ and 2.98 and $5.74 \mu_{\text{B}}$ for $x = 0.10$, respectively [11]. Our μ_{eff} values for isolated spins are close to the value predicted by the random substitution model, whereas it is significantly higher for grouped spins for $x = 0.10$.

Our susceptibility data indicate the presence of Co^{2+} clusters with antiferromagnetically correlated moments. The Θ values obtained from the fitting with equation (1) to the experimental data are significantly higher for $x = 0.10$ as compared to $x = 0.05$. This indicates a larger number of grouped nearest neighbour Co^{2+} ions for $x = 0.10$. The new feature which we are reporting in this work is the correlation between the presence of grouped Co^{2+} ions for $x = 0.10$ and the anomalous peak broadening of the x-ray diffraction profiles. In wide bandgap semiconductors like (Ga, Mn)N and (Ga, Mn)As, a percolation threshold of $x_{\text{c}} = 0.20$ has been predicted [10]. There is no published report on the threshold value x_{c} for the (Zn, Co)O system. We are, however, aware of an unpublished result [20] which suggests that the clustering of Co atoms in (Zn, Co)O takes place for $x \geq 0.10$ but not for $x \leq 0.05$. This implies that x_{c} would lie in the range of $0.05 < x_{\text{c}} < 0.10$. The fact that anomalous peak broadening set in for $x \geq 0.10$ in our samples seems to be in excellent agreement with theoretical predictions. We believe that the clustering of Co^{2+} ions introduces strain in the matrix, which in turn leads to anomalous x-ray diffraction peak broadening. These strains may promote enhanced overlap of p-d orbitals, and hence enhanced super-exchange interaction parameter, J . Such an enhancement in J is reflected through higher Θ values for $x = 0.10$ (see table 1) as compared to that for $x = 0.05$. The strain induced enhancement of J may provide the driving force for the spinodal decomposition process postulated by Sato *et al* [10].

4. Conclusion

In summary, our investigations, though they indicate enhancement of the solubility limit of Co in ZnO matrix, meeting the criteria for room temperature ferromagnetism in DMS, do not show any ferromagnetic ordering down to 2 K. Magnetic measurements reveal both paramagnetic and antiferromagnetic correlations among the Co ions. These antiferromagnetically ordered magnetic clusters however produce strain in the lattice, which is clearly observed

from anomalous x-ray diffraction peak broadening. The anomalous strain could be experimental evidence for the spinodal decomposition proposed theoretically in DMSs.

Acknowledgments

CR and DP gratefully acknowledge discussions with Professor T V Ramkrishnan, FRS, on the likely role of strain in the DMS systems. UGC-DAE Consortium for Scientific Research (CSR), Indore, is acknowledged for support. DST, Government of India, is acknowledged for funding the 14T-PPMS-VSM at CSR, Indore.

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