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SUPERCONDUCTIVITY IN METALLIC GLASSES

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I. INTRODUCTION

The earliest studies of amorphous superconductors were carried out twenty-five years ago on thin films of simple metals prepared by vapor deposition on a cryogenic substrate^(1,2). Bergmann⁽³⁾, and the author⁽⁴⁾ have surveyed some of the properties of such materials in recent reviews. In the past ten years, studies of amorphous superconductors have been extended to transition metals^(5,6), and most recently to metallic glasses^(4,6,7). The latter materials are prepared by rapid quenching of liquid metallic alloys using techniques originally developed by Duwez⁽⁸⁾.

It would be both difficult and repetitive to completely review this field in the limited space available here. The interested reader is referred to the above mentioned articles for a more complete survey. In the present article, attention will be focused on recent developments. The main results of earlier work will be summarized where convenient.

II. ELECTRONIC STRUCTURE AND SUPERCONDUCTIVITY

McMillan⁽⁹⁾ has given a solution to the strong-coupling equations of Eliashberg which he obtained using numerical techniques together with the measured phonon spectrum of niobium. Using his solution, the superconducting transition temperature is given by

$$T_c = [\theta_D/1.45] \exp - \left[\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right] \quad (1)$$

In this expression, θ_D is the Debye temperature (or suitably averaged phonon frequency), μ^* the effective Coulomb coupling constant, and λ the dimensionless electron phonon coupling constant. McMillan expresses λ in terms of other microscopic parameters as

$$\lambda = \frac{D(0)\langle I^2 \rangle}{M\langle \omega^2 \rangle} \quad (2)$$

where $D(0)$ = electron density of states at the Fermi level

$\langle I^2 \rangle$ = average squared electron-ion matrix element

M = ionic mass

$\langle \omega^2 \rangle$ = mean square phonon frequency (defined by McMillan)

Although the phonon spectrum and Eliashberg function $\alpha^2(\omega)F(\omega)$ of amorphous metals may differ from that used by McMillan to obtain eqn. (1), one would still expect that the corresponding expression for T_c in amorphous alloys will have a similar form^(4,10). Therefore, eqns. (1) and (2) still provide a convenient framework in which to analyze the systematics of superconductivity in amorphous metals.

A. Simple Metals

The occurrence of superconductivity in amorphous simple metals can be understood by using an extension of the nearly free electron model. Ziman has applied this model to liquid metals⁽¹¹⁾. Bergmann⁽³⁾ has given an extensive account of the experimental evidence which supports such a picture in the case of superconducting amorphous simple metals. In particular, the model correctly predicts the Hall coefficient⁽¹²⁾ R_H , electrical resistivity $\rho(T)$, and temperature dependence of $\rho(T)$ for the majority of simple metals⁽¹³⁾. Rainer and Bergmann⁽¹⁴⁾ have also discussed the calculation of $\langle I^2 \rangle$ and $\langle \omega^2 \rangle$. They argue that disorder results in an enhancement of low frequency contributions to electron-phonon scattering and consequently to enhanced values of λ . They conclude that amorphous metals should tend to be strong-coupling ($\lambda > 1$) superconductors.

Experimental evidence obtained from superconductive tunneling indeed supports this conclusion^(3,15,16).

The author⁽⁴⁾ has attempted to explain the systematics of superconductivity in simple amorphous metals by assuming that the strong disorder leads to a nearly spherical Fermi surface. A simple jellium model was used to determine the variation of λ with a few simple parameters such as valence Z , atomic volume v_a , and ionic mass M . In the jellium model, the ionic plasma frequency $\Omega_p = \left(\frac{4\pi N e^2}{M} \right)^{1/2}$ (where N = density of ions) is a natural scale for phonon frequencies. A plot of the dimensionless ratio $[k_B T_c / \hbar \Omega_p]$ for amorphous simple metals as a function of average valence Z is shown in Fig. 1 and suggests remarkably systematic relationship. Roughly speaking, this ratio is a measure of the exponential factor on the right hand side of eqn. (1), and thus a measure of λ . Using Z , v_a , and M as input parameters in the jellium model, together with the Heine-Abarenkov pseudopotential form factors for simple metals, a simple model calculation of λ was carried out⁽⁴⁾. It was found that λ is determined mainly by valence. These results are illustrated in Fig. 2.

Fig. 1. Variation with valence of the superconducting transition temperature of simple amorphous metals. The values of T_c are normalized to the characteristic bare phonon temperature $[\hbar \Omega_p / k_B]$ of each material.

In crystalline metals, the influence of long range order on electronic band structure results in large deviations of the electronic density of states $D(\epsilon)$ from the free electron model. These deviations in turn influence electron-phonon scattering, and electron screening. The absence of long range order in amorphous metals tends to eliminate these band structure effects and leads to a free electron-like Fermi surface. As a result, the jellium model gives a much better description of amorphous as compared to crystalline simple metals which are not well described by the jellium model⁽⁴⁾. The microscopic origin and systematics of superconductivity are correspondingly easier to understand in amorphous metals.

B. Transition Metals

The superconducting properties of amorphous transition metals are governed mainly by the partially occupied d-states. In contrast with the case of simple metals, one cannot use the free electron approach to understand these materials. The d-electrons are perhaps best described as being tightly bound. Friedel⁽¹⁸⁾, Cyrot-Lackmann⁽¹⁹⁾, and others have discussed the tight-binding approximation TBA as it applied to liquid transition metals. Recently, Varma and Dynes⁽²⁰⁾ have analyzed superconductivity in crystalline transition metals using an extension of the TBA method to include the nonorthogonality of atomic d-orbitals centered on neighboring atoms. They find that the d-band contribution $D_d(\epsilon_F)$ to $D(\epsilon_F)$ is the most important microscopic parameter which determines λ . Their argument shows that the ratio $[<I^2> / <\omega^2>]$ in eqn. (2) should be roughly constant within a given d-band (i.e. the 4d or 5d band).

Applying the Varma-Dynes analysis to the case of amorphous transition metals requires information regarding the behavior of $D_d(\epsilon)$. Several experimental techniques have been used to obtain such information. These include measurements of magnetic susceptibility, low temperature specific heat, x-ray and ultraviolet photoemission spectra, and also indirect deduction of $D(\epsilon_F)$ from upper critical field, $H_{c2}(T)$, measurements. Magnetic susceptibility measurements on metallic glasses of the series $(\text{Mo}_{1-x}\text{Ru}_x)_{80}\text{P}_{20}$ have been reported⁽²¹⁾. The temperature independent contribution to the susceptibility, χ_0 , was found to be large and to decrease with x as shown in Fig. 3. If one

Fig. 2. Values of the electron-phonon coupling constant λ calculated using a simple jellium model with Z , M , and v_a as input parameters. See ref. 4 for details.

assumes that the Pauli paramagnetic contribution associated with $D(\epsilon_F)$ dominates χ_0 , then this can be interpreted to indicate a smooth decrease of $D(\epsilon_F)$ with increasing x as shown in the figure. Also shown in the figure is the variation of T_C with x for these metallic glasses and the variation of T_C with x for amorphous $\text{Mo}_{1-x}\text{Ru}_x$ thin films prepared by cryoquenching by Collver and Hammond⁽⁴⁾. These results suggest a direct relationship between $D(\epsilon)$ and T_C . Recent low temperature specific heat measurements⁽⁴⁾ on the same series of metallic glasses have confirmed the decrease of $D(\epsilon)$ with x . The absolute values of $D(\epsilon)$ obtained from the coefficient of the linear contribution to c_p are in remarkably good agreement with $D(\epsilon)$ values estimated from χ_0 ⁽⁴⁾. Schroeder et al⁽²²⁾ and Amamou and the author⁽²³⁾

have used XPS and UPS measurements to gain insight into the variation of $D(\epsilon)$ for $\epsilon < \epsilon_F$. Typical results are shown in Fig. 4 for the alloy $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{80}\text{B}_{20}$. The data suggest that a general loss of structure in $D(\epsilon)$ occurs on going from the crystalline to the amorphous state. It also suggests that $D(\epsilon)$ is characterized by a broad maximum with the peak occurring somewhat below the Fermi level of the alloy. In other words, $D_d(\epsilon)$ appears to vary rather smoothly with d-band occupation exhibiting a maximum for a roughly half filled d-shell. The variation of T_C observed by Collver and Hammond⁽⁴⁾ for cryoquenched films of transition metals and alloys of neighboring metals of the 4d series is shown in Fig. 5. The variation of T_C through a similar broad maximum is consistent with the Varma-Dynes analysis if the density of

Fig. 3.(top) The temperature independent contribution χ_0 to the magnetic susceptibility and corresponding density of states $D(0) = 2 \mu_B^2 \chi_0$ estimated by assuming χ_0 is dominated by Pauli paramagnetism.

(bottom) The variation of T_c for the same alloys along with that observed by Collver and Hammond for $\text{Mo}_{1-x}\text{Ru}_x$ thin films.

states $D_d(\epsilon)$ has the above characteristics. In contrast, the Matthias curve for crystalline transition metals is shown in the same figure. In the crystalline case, a rapid variation of $D_d(\epsilon_F)$ with d-band occupation is predicted by band structure calculations^(24,25) and confirmed by specific heat measurements^(9,20,26). Those crystalline metals and alloys for which ϵ_F falls near a sharp maximum in $D(\epsilon)$ have high T_c values as expected in the Varma-Dynes model. The crystalline to amorphous transition washes out the d-band structure and thus leads to a smoother variation of both $D_d(\epsilon)$ and consequently T_c (4).

C. Effects of Disorder on Superconductivity

In amorphous metals, essentially every atom can act as a scattering center for conduction

electrons. This is due to the highly disordered atomic arrangement. In the case of simple metals, the atomic potential is comparatively weak. The Ziman theory of liquid metals⁽¹¹⁾ is premised on the assumption of weak scattering and as such neglects multiple scattering effects. Using the simplest solution to the Boltzmann equation, one can estimate the electronic mean free path for amorphous simple metals directly from measurements of $\rho(T)$. At cryogenic temperatures, $\rho(T \rightarrow 0)$ ranges from 25-100 $\mu\Omega\text{cm}$ for typical simple metals. From

$$\rho = \frac{mv_F}{ne^2 \ell_e} \quad (3)$$

and free electron values for the Fermi velocity,

Fig. 4. The x-ray photoemission spectrum of $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{80}\text{B}_{20}$ shows the width and shape of the d-band. UPS spectra are given in ref. 22.

v_F , one obtains an electron mean free path ℓ_e which ranges from several times the interatomic distance d up to roughly $10d$. The Ziman model is expected to break down when $\ell_e \approx d$. Mott has termed this the electron diffusion⁽²⁷⁾ or strong scattering regime and predicts that this regime is approached when $\rho \gtrsim 300 \mu\Omega\text{cm}$. Resistivities of this order are in fact observed in amorphous transition metals where eqn. (3) gives values of $\ell_e \approx d$. It should be noted that still larger values of ρ (i.e. $\rho \gtrsim 3000 \mu\Omega\text{cm}$) are expected to result in Anderson localization of electronic states⁽²⁸⁾.

The small value of ℓ_e typically found for amorphous metals^(27,28) has important consequences for superconductivity. The purity parameter $\lambda_p = (\xi_0/\ell_e)$ where ξ_0 is the zero temperature coherence length in the clean limit ($\xi_0 = \frac{\hbar v_F}{\pi \Delta}$ ⁽²⁹⁾) is exceptionally large, $\lambda_p \sim 10$ - 100 , for amorphous metals. Thus, amorphous metals are a case of superconductivity in the extreme dirty limit⁽²⁹⁾. In this limit the coherence length becomes

$$\xi_d(t) = 0.85 [\xi_0(T)\ell_e]^{1/2} t^{-1/2} \quad (4)$$

where t is the reduced temperature $t = \left(\frac{T-T_c}{T_c}\right)$,

while the penetration depth is given by⁽²⁹⁾

$$\lambda_d(t) = 0.615 \lambda_L(0) \lambda_p^{1/2} t^{-1/2} \quad (5)$$

where $\lambda_L(0)$ is the London penetration depth. For amorphous metals $\xi_d(0)$ is in the range 30 - $100 \text{ \AA}$ while $\lambda_d(0)$ is of the order of $1 \mu\text{m}$. The Ginzburg-Landau parameter $\kappa = (\lambda/\xi)$ is of order 10 - 100 ^(30,31).

As a consequence of the above facts, amorphous superconductors have a large upper critical field $H_{c2}(T)$ ^(30,31), small lower critical field $H_{c1}(T)$ ⁽³⁰⁾, and exhibit large critical fluctuations⁽³²⁾. The upper critical field behavior is particularly interesting and has recently been studied over an extended range of t for amorphous transition metal alloys by Tenhover, Tsuei, and the author⁽³¹⁾. Examples of these data are shown

Fig. 5. The variation of T_c with average group number for thin amorphous films of 4d transition metals and alloys. For comparison, the variation of T_c in corresponding crystalline metals and alloys is shown.

in Fig. 6. The theoretical calculation of $H_{c2}(T)$ in the dirty limit has been carried out by several authors^(33,34,35). Corrections to the basic theory for spin orbit scattering⁽³⁵⁾, paramagnetic limiting⁽³⁶⁾, strong-coupling⁽³⁷⁾, an anisotropy effects⁽³⁸⁾ have been successful in explaining most data on known superconductors. Exceptions to this included recent results on ultra thin films⁽³⁹⁾, and the data in Fig. 6. The figure shows the theoretical curves for $\kappa(t) = (H_{c2}(T)/H_{c2}^L(0))$ where $H_{c2}^L(0)$ is obtained by linear extrapolation. By letting the spin-orbit coupling parameter $\lambda_{so} \rightarrow \infty$, one obtains the highest appropriate theoretical prediction for $\kappa(t)$. The theory is clearly inadequate to explain the persistent linearity of $\kappa(t)$ at low t . Combining the data of Fig. 6 with all other available data on amorphous reveals that the discrepancy with theory systematically increases with increasing normal state resistivity ρ ⁽³¹⁾. Values of ρ of the order of 200 $\mu\Omega\text{cm}$ are observed

for the alloys in Fig. 6. On this basis, it is suggested that this behavior is related to strong-electron scattering effects and the tendency toward electron localization. Such effects would also be expected for the case of ultrathin films⁽³⁹⁾.

The topological and chemical disorder in amorphous transition metal alloys should result in large fluctuations in the atomic environment. In the TBA model of the d-band, one would expect large fluctuations in the two center overlap integral⁽¹⁷⁾

$$J = \int \phi_d^* (\vec{r}-\vec{r}_1) V_a (\vec{r}-\vec{r}_1) \phi_d (\vec{r}-\vec{r}_2) d^3\vec{r} \quad (6)$$

where $\vec{r}_1$ and $\vec{r}_2$ are the position vectors of neighboring atoms, V_a the atomic potential, and ϕ_d an atomic d-orbital. Roughly J depends on $|\vec{r}| = |\vec{r}_2 - \vec{r}_1| = \ell$ as

$$J(\ell) = J_0 e^{-\ell q_0} \quad (7)$$

Fig. 6. The reduced upper critical field $h(t) = H_{c2}(T)/H_{c2}^L(0)$ vs. t for several transition-metal-base metallic glasses. Dashed lines are theoretical curves.

where q_0 is the Slater coefficient for decay of the d-orbital. The d-band width is of order

$$W_d \approx 2z \langle J \rangle \langle \cos\theta \rangle \quad (8)$$

where z is the first neighbor coordination number. From the atomic pair correlation function of metallic glasses⁽⁴¹⁾ (e.g. $(W_{0.5Ru_{0.5}})_{80}B_{20}$) we estimate the mean value of ℓ to be $\bar{\ell} \approx 3\text{\AA}$ while fluctuations in ℓ are of order $\Delta_\ell \approx 1.0\text{\AA}$. Taking $J(\bar{\ell}) \approx 1\text{eV}$, and $q_0 \approx 1\text{\AA}^{-1}$ ⁽⁴⁰⁾ gives $J_0 \sim 10\text{--}30\text{ eV}$. Thus the relative fluctuations in $J(\ell)$ are typically

$$\left(\frac{\Delta J}{W_D}\right) \approx \left(\frac{\Delta_\ell}{W_D}\right) \left| \frac{\partial J(\ell)}{\partial \ell} \right|_{\ell=\bar{\ell}} = \frac{q_0 \Delta_\ell}{z \langle \cos\theta \rangle} \quad (9)$$

The factor $\langle \cos\theta \rangle$ accounts for the directional properties of the d-orbitals and for strongly directional d orbitals we could take $z \langle \cos\theta \rangle \sim 2$. Thus we estimate

$$(\Delta_J/W_D) \sim \frac{1}{2} \approx \frac{1}{2} \quad (10)$$

We see that topological disorder alone can produce substantial fluctuations in local environment.

Chemical disorder (e.g. fluctuations in Mo-Mo, Mo-Ru, and Ru-Ru coordination) will produce additional diagonal disorder. One might expect to approach the Anderson localization criteria for the d-band of a transition metal glass.

The above discussion ignores s-d (p-d) hybridization which can be parametrized by a parameter J_{sd} . If $J_{sd} \rightarrow 0$, then the d-electrons would be decoupled from the s,p-electrons and could exhibit localization for sufficiently high disorder. For finite J_{sd} , the localization would tend to be suppressed by the greater spatial extent of s,p orbitals. This interesting problem has important consequences for superconductivity since the d-electron time and spatial correlation effects play an important role in the microscopic theory of the inhomogeneous superconducting state.

III. ATOMIC SCALE STRUCTURE AND MORPHOLOGY OF AMORPHOUS SUPERCONDUCTORS

The simplified picture of the d-band density of states $D_d(\epsilon)$ described in section II B. ignores the influence of metalloid elements (e.g. B, P, etc.) on electronic properties. Recent studies⁽⁴²⁾ suggest the metalloid elements play a significant

Fig. 7. Nearest neighbor distance d vs. composition for $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$, $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{Si}_x$, and $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{1-x}\text{P}_x$ metallic glasses. Distances were determined from the Debye formula. (see ref.42)

Fig. 9. Linear coefficient for low temperature specific heat vs. composition for $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$ metallic glasses. The open circles were deduced from critical field data and eqn. (11). The crosses are taken directly from specific heat data.

Fig. 8. Electrical resistivity vs. composition for $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$ and $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{Si}_x$ metallic glasses.

role in both the atomic scale structure and electronic properties of metallic glasses. This is best illustrated by the example of

$(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$ glasses which can be obtained over the composition range $0.10 < x < 0.24$. Several properties of these alloys have been found to change discontinuously with composition near $x = 0.18$.

Some examples shown in Figs. 7 and 8 are the average nearest neighbor distance and the electrical resistivity. The former is found to increase with x for $x < 0.18$ and decrease for $x > 0.18$. The latter is nearly independent for x for $x < 0.18$ and increases rapidly for $x > 0.18$ (from $\sim 120 \mu\Omega\text{cm}$ to $250 \mu\Omega\text{cm}$). Another example of such behavior is also shown for the metal-metalloid glasses

$(\text{Pd}_{0.5}\text{Ni}_{0.5})_{1-x}\text{P}_x$. The metallic glasses $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{Si}_x$ are similar but show no discontinuities. The critical field gradient $(dH_{c2}/dT)_{T_c}$ and electrical resistivity can be used together to determine the electronic density of states $D(\epsilon_F)$ using the relation⁽⁴³⁾

$$\left(\frac{dH_{c2}}{dT}\right)_{T=T_c} = -4.48 \times 10^4 \gamma \rho \text{ (OeK}^{-1}\text{)} \quad (11)$$

where γ is the equivalent linear coefficient in the electronic heat capacity (in $\text{erg cm}^{-3}\text{K}^{-2}$) and ρ is in units of (Ωcm) . Values of γ so obtained are plotted for $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$ glasses in Fig. 9. Specific heat data⁽⁴⁴⁾, available for two of the alloys, is included in the figure and agrees extremely well with the γ deduced from H_{c2} . A precipitous drop in γ vs. x occurs near $x = 0.18$ with $\gamma \approx 4 \text{ (mJ/mole-K}^2\text{)}$ for $x < 0.18$ and $\gamma \approx 2 \text{ (mJ/mole-K}^2\text{)}$ for $x > 0.18$. We conclude that $D(\epsilon_F)$ drops by roughly a factor of 2 over this narrow composition interval.

All of the above facts suggest some type phase transition or dramatic structural change near $x = 0.18$. The above observations are explained by assuming two different amorphous phases with compositions $x < 0.18$ and $x > 0.18$. Near $x = 0.18$, the alloy would contain both phase in comparable proportions. The technique of small angle x-ray scattering SAS was used to obtain evidence of the proposed phase separation⁽⁴⁵⁾. Typical small angle scattering spectra are shown in Fig. 10. Curves A, B, C, and D show spectra for as quenched foils with $x = 0.12, 0.14, 0.18$, and 0.20 respectively.

A clear feature in the SAS intensity is observed for scattering vector $K \sim 0.3$. This feature is most pronounced for $x = 0.18$ and can be interpreted by assuming a phase segregation into domains of characteristic size $\sim 10\text{-}15\text{\AA}$ with a typical inter-domain distance of $20\text{-}30\text{\AA}$.

Results of neutron irradiation studies on $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{82}\text{B}_{18}$ have previously been reported⁽⁴⁶⁾. The SAS spectrum of a neutron irradiated sample is shown by curve E. The sample was irradiated to a total fluence of 10^{19} n/cm^2 of fast neutrons (1 Mev) over a period of several days. The overall increase in small angle scattering reflects an increase of point defects during irradiation. The large increase in the broad maximum near $K \sim 0.3$ suggests enhanced phase separation. This can be understood since the increased point defect concentration should enhance diffusion at room temperature⁽⁴⁷⁾.

It is clear that both the electronic structure and atomic scale structure of these metallic glasses are strongly influenced by the phase separation discussed above. On the other hand, the superconducting properties of these materials should reflect only the average properties of the material since the scale of phase separation $10\text{-}25\text{\AA}$ is substantially smaller than the coherence length of the superconductor $\xi_d(0) \approx 50\text{\AA}$. However, it may be possible to produce a coarser phase separation by thermal aging of the glass. This would result in an intrinsically inhomogeneous superconducting material. An example of clear phase separation on a much larger scale has been observed in a novel family of superconducting metallic glasses $(\text{Pb}_{1-y}\text{Sb}_y)_{1-x}\text{Au}_{x_0}$ ⁽⁴⁸⁾. Here, phase separation on a scale of $\sim 1000 \text{\AA}$ leads to an inhomogeneous superconducting material in which both phases percolate throughout the sample.

IV. SUMMARY

This article, as mentioned in the introduction, was not intended to be a comprehensive review. The questions raised in the article serve to emphasize that the electronic structure of superconducting metallic glasses is far from being well understood. More generally, the electronic and atomic scale structure of metallic glasses may be considerably more complex than previously recognized. Emphasis has been given to several current problems in the

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Fig. 10. Small angle scattering intensity, $J(K)$, of $(\text{Mo}_{0.6}\text{Ru}_{0.4})_{1-x}\text{B}_x$ alloys. Curves A, B, C, and D are for compositions $x = 0.12, 0.14, 0.18, 0.20$ respectively. Curve E is for a neutron irradiated specimen with $x = 0.18$. A total fluence of 10^{19} n/cm² of fast (1 MeV) neutrons was accumulated over a period of 2 days.

study of amorphous superconductors. Hopefully, future research will provide a deeper insight into the nature of these novel materials.

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