Effects of valence fluctuation and pseudogap formation on phonon thermal conductivity of Ce-based compounds with \(\epsilon\)-TiNiSi-type structure

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We have measured the thermal conductivity of isostructural compounds CePtSn, CeNiSn, CeRhSb, and CeRhAs with the orthorhombic \(\epsilon\)-TiNiSi-type structure. It is found that the phonon thermal conductivity is reduced in a systematic way with increasing Kondo temperature \(T_K\). The scattering of phonons by valence fluctuations should play a dominant role in such a reduction. The gap formation in the electronic density of states enhances the phonon thermal conductivity significantly in CeRhAs with a gap width of 280 K, while it is weak in CeNiSn or CeRhSb with a pseudogap of 20–30 K. A phenomenological model is proposed for the unusual temperature dependence of phonon thermal conductivity by taking account of the strong dependence of the electron-phonon scattering rate on both \(T_K\) and the energy gap.

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I. INTRODUCTION

Recently, many efforts were devoted to explore materials with high thermoelectric efficiency exceeding that of the state-of-the-art systems based on Bi-Te alloys. One of the central issue in this research field is how to reduce the thermal conductivity \(\kappa\), maintaining good electrical conductivity. Slack has proposed the concept “phonon glass and electron crystal (PGEC)” to reconcile these incompatible conditions.\(^1\) This concept insists that an extremely short phonon mean free path (mfp) caused by a phonon glassy state leads to a significant reduction of the phonon thermal conductivity \(\kappa_{ph}\), while the longer charge carrier mfp is secured in a crystalline part of the material. According to this concept, one has to add an extra phonon scattering source, and several good possibilities such as “rattling”\(^2,3\) and “disorder”\(^4\) are suggested. In some clathrates\(^2\) (e.g., Eu\(_4\)Ga\(_{16}\)Ge\(_{30}\)) and in filled skutterudites\(^3\) (e.g., CeFe\(_2\)Sb\(_{12}\)), a rattling motion of a rather heavy atom caged in a rigid polyhedron causes an extra phonon scattering while charge carrier well conduct via the polyhedron’s frame. The atomic disorder in NaCo\(_2\)O\(_4\) can be considered as point defects for phonons. In this compound, a layer composed of Na atoms and vacancies is sandwiched by electrical conducting CoO\(_2\) layers.\(^4\)

It has been claimed that phonon scattering by a valence fluctuating (VF) state is also a promising process to reduce \(\kappa_{ph}\).\(^5,7\) For example, in the skutterudite Ru\(_0.3\)Pd\(_{0.7}\)Sb\(_3\), the VF between Ru\(_{3+}\) and Ru\(_{4+}\) states is believed to scatter heat carrying phonons.\(^6,7\) But the role of the phonon-VF (ph-VF) scattering in \(\kappa_{ph}\) is less understood compared to that of the rattling and the atomic disorder, probably due to the absence of sophisticated experiments for VF compounds. Therefore it stimulated us to carry out systematic experiments of \(\kappa\) of isostuctural VF compounds, Ce-based VF compounds with Ce\(^{3+}\) and Ce\(^{4+}\) states showing good electrical conductivity are characterized by the Kondo temperature \(T_K\), which ranges from 50 to 1000 K. Aiming to obtain better insight into the influence of the ph-VF scattering with a change of \(T_K\), we focus on the isostuctural systems CePtSn, CeNiSn, CeRhSb, and CeRhAs, all of which crystallize into the orthorhombic \(\epsilon\)-TiNiSi-type structure. We further discuss on the possibility of the PGEC state.

CePtSn is a metallic system where Ce ions are in the trivalent state with \(T_K\approx 10\) K, and undergoes two magnetic phase transitions at 7.5 K and 5.0 K.\(^8\) CeNiSn and CeRhSb are VF semimetals with \(T_K\approx 50\) and 90 K, respectively.\(^9\) On cooling below a characteristic temperature \(T^*\), of 15 K for CeNiSn (20 K for CeRhSb), a pseudogap of 20 K (30 K) is formed leaving a residual density of states at the Fermi level, \(D_{Fg}(E_F)\).\(^10,16\) CeRhAs with \(T_K=1350\) K is a VF semiconductor where a pseudogap of 280 K opens below \(T^*=370\) K.\(^19,20\) The gap formation in CeRhAs is intimately related to successive phase transitions accompanying lattice modulations at \(T_1=370\) K, \(T_2=235\) K, and \(T_3=165\) K.\(^20\) The rapid development of the pseudogap occurs below \(T_3\). From these facts, one can expect that the effect of ph-VF scattering on \(\kappa_{ph}\)'s of the four compounds primarily depends on the value of \(T_K\), without perturbing significantly other phonon-scattering processes.

It is reported that \(\kappa_{ph}\) of CeNiSn and CeRhSb is enhanced when the pseudogap is formed below \(T^*\).\(^21,23\) This enhancement was attributed to the increase of the phonon mfp by the diminishing of the charge carrier density, in analogy to high-\(T_C\) superconductors below the superconducting transition temperatures \(T_C\). However, a systematic study of \(\kappa_{ph}\) by changing \(T^*\) has not been reported so far. Thus, the second aim in this study is to investigate the relationship between the enhancement of \(\kappa_{ph}\) and the magnitude of \(T^*\). In this paper, we present experimental results of \(\kappa\) for CePtSn, CeNiSn, CeRhSb, and CeRhAs, and discuss the effect of both the VF and the pseudogap formation on \(\kappa_{ph}\).

II. EXPERIMENTAL METHODS

Single crystalline samples of CePtSn and CeNiSn were grown by the Czochralski pulling method in a radiofrequency furnace. On the other hand, the Bridgman technique using a sealed tungsten crucible was employed to prepare single crystals of CeRhSb and CeRhAs with high vapor pressures. Details of the crystal growth were reported in separate
The typical sizes of the samples were 0.6 m m 3 . The separation measurement of a standard steel sample purchased from NBS. In this study the thermal gradient ∆Q was applied along the orthorhombic b axis for all compounds. The typical sizes of the samples were 0.6×0.6×3 mm 3 . The electrical resistivity ρ along the b axis was measured in the range 1.5–500 K by a conventional four-probe method to estimate the electronic contribution to κ.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show ρ(T) and κ(T) of all compounds studied in this work, respectively. As mentioned in the Introduction, metallic ρ(T) for CePtSn, semimetallic ones for CeNiSn and CeRhSb, and semiconducting one for CeRhAs are clearly observed. The present κ(T) values of CePtSn are larger than those of the previous report 22 measured between 1.5 K and 100 K. This difference amounting to 15% at 40 K cannot be adjusted by multiplying either data with an appropriate factor and is probably caused by the better sample quality in this study than that used in the previous one. In the case of CeNiSn or CeRhSb, the difference in κ between the present value and the previous one 22 is at most 5%, which, however, can be adjusted by multiplying either data by an appropriate factor. Therefore, these differences are ascribed to geometrical uncertainties. The thus combined data are given in Fig. 2 for CeNiSn and CeRhSb. For CePtSn, a shoulderlike structure around 40 K is the main feature in κ(T). This structure is significantly reduced in κ(T)’s of CeNiSn and CeRhSb with an increase of T K . On going from CePtSn, CeNiSn, CeRhSb, to CeRhAs along the enhancement of T K , κ above 150 K is also considerably reduced by an order of magnitude. These facts signal a strong effect of the VF on κ(T). At low temperatures, a highly contrasted effect of the pseudogap formation is revealed by comparing κ(T) of CeRhAs with those of CeNiSn and CeRhSb. While a pronounced enhancement of κ below T 3 =165 K is observed in CeRhAs with T* of 370 K, CeNiSn and CeRhSb both of which possess T* of 15–20 K exhibit rather faint ones below 10 K for CeNiSn and 20 K for CeRhSb, respectively. For CeRhAs, the jump in κ(T) at T 3 =165 K corresponds to the occurrence of a structural phase transition with the lattice modulation.

The reduced Lorenz number L/L 0 is given in the inset of Fig. 2. The Lorenz number, L is defined by κρ/T, and L 0 is the Sommerfeld value of 24.5 nW Ω K −2 . The L/L 0 of CeRhAs increases rapidly on cooling and reaches a value as high as 5×10 3 at 4.2 K, reflecting the semiconducting behavior of ρ. On the contrary, L/L 0 ’s of other compounds are situated between 2 and 20 in the measured temperature range, which is ascribable to the metallic behavior of ρ. It should be noted that the values of L/L 0 ’s for CeNiSn, CeRhSb, and CeRhAs are larger than those of typical heavy-fermion compounds such as CeCu 6 and CeRu 2 Si 2. 25,26 In CeRu 2 Si 2 , the inelastic scattering of charge carriers by 4f spin fluctuations leads to the reduction of L/L 0 below 1. 26 The large L/L 0 indicates that the dominant heat carriers are phonons, and spin scattering of charge carriers would not play a significant role in L/L 0 . Therefore, in these VF systems one can extract a precise phonon contribution, and it guarantees a reliable discussion on the effects of the VF and the pseudogap formation on κ ph . This criterion may be applied also for CePtSn at least up to 100 K, above which L/L 0 has a rather small value.

The temperature dependence of κ ph for all compounds are shown in Fig. 3. The data of κ ph were obtained by subtracting the electronic contribution κ el from the measured data. Thereby, the validity of the Wiedemann-Franz law κ el =L 0 T/ρ is assumed, and κ el is calculated by using the data of ρ(T) shown in Fig. 1. For CePtSn, the shoulderlike structure in κ(T=40 K) (see Fig. 2) is converted to a broad maximum in κ ph (T=30 K) in Fig. 3. This maximum may represent the crossover from dominating phonon-phonon (ph-ph) scattering above about 30 K to electron-phonon (el-ph) interaction below 30 K. The broad maximum in κ ph (T)
FIG. 3. The temperature dependence of $\kappa_{ph}$ for CePtSn, CeNiSn, CeRhSb, and CeRhAs. The solid lines are $\kappa_{min}$'s of respective compounds. The dashed and dash-dotted lines represent the $T^2$ and the $T^{-1}$ dependences, respectively.

of CeNiSn and CeRhSb with higher values of $T_K$ is depressed compared to that for CePtSn. At temperatures above 165 K, $\kappa_{ph}$ is systematically reduced on going from CeNiSn, CeRhSb, to CeRhAs in line with the enhancement of $T_K$. It should be noted that the lattice modulation may contribute to the reduction of $\kappa_{ph}$ of CeRhAs as well.

We discuss now the origin of the reduction of $\kappa_{ph}$ with increasing $T_K$. At high temperatures, $\kappa_{ph}$ is dominated by ph-ph scattering, and thus depends essentially on the Debye temperature $\Theta_D$. In isostructural compounds with the same ph-ph scattering rate, $\kappa_{ph}$ becomes larger with increasing $\Theta_D$. Since $\Theta_D$'s of none of the present compounds are reported, we use the $\Theta_D$'s of the La counterparts; LaNiSn ($=228$ K) and LaRhSb ($=275$ K). If $\Theta_D$'s of CeNiSn and CeRhSb are assumed to be those of the La counterparts, $\kappa_{ph}$ of CeRhSb is expected to be larger than that of CeNiSn at high temperatures, which, however, contradicts the experimental result. The second important process of phonon scattering at high temperatures is that by isotope atoms; the mechanism of which is similar to that of point defect scattering. The scattering rate associated with the isotope effect can be expressed by $\tau_{iso}^{-1} = D_{iso} \omega^3 = (V/4\pi D_{ph}^3) \Gamma_{AV} \omega^3$, where $V$ is the unit cell volume, $v_{ph}$ the average phonon velocity, $\Gamma_{AV}$ the averaged scattering parameter given in Eq. (1), and $\omega$ the phonon frequency. The $v_{ph}$ is obtained from $v_{ph} = k_B \Theta_D / \hbar \sqrt{6 \pi^2 n}$, where $k_B$ is the Boltzmann constant, $\hbar$ the Planck constant divided by $2\pi$, and $n$ the number of atoms per unit volume. The $n$ is obtained by using lattice constants listed in Table I. The $\Gamma_{AV}$ for CeNiSn is determined as follows:

$$\Gamma_{AV}(\text{CeNiSn}) = \frac{1}{3} \left( \frac{m_{Ce}}{m_{AV}} \right)^2 \Gamma(\text{Ce}) + \frac{1}{3} \left( \frac{m_{Ni}}{m_{AV}} \right)^2 \Gamma(\text{Ni}) + \frac{1}{3} \left( \frac{m_{Sn}}{m_{AV}} \right)^2 \Gamma(\text{Sn}),$$

where $m_X$ means the mass of an atom denoted by $X$, $m_{Xi}$ that of an isotope $X$ atom of type $i$, and $c_i$ is the concentration of the atom denoted by $Xi$. The $\Gamma_{AV}$ of CeRhSb is calculated by the same method. Using the isotope atoms tabulated by Strominger et al., one obtains $D_{iso} = 42.5 \times 10^{-44}$ ($s^3$) for CeNiSn and $3.87 \times 10^{-44}$ ($s^3$) for CeRhSb. Therefore, the reduction of $\kappa_{ph}$ due to the isotope effect in CeNiSn is an order of magnitude larger than that in CeRhSb. This would lead finally to a larger value of $\kappa_{ph}$ for CeRhSb in comparison to CeNiSn. Hence, neither ph-ph scattering nor the isotope effect can explain the experimental relation $\kappa_{ph}(\text{CeNiSn}) > \kappa_{ph}(\text{CeRhSb})$ as shown in Fig. 3 for high temperatures. Thus, the most probable mechanism in reducing $\kappa_{ph}$ of CeRhSb below that of CeNiSn should be the stronger ph-VF scattering in CeRhSb. The above brief discussion combined with the overall systematic trend with $T_K$ leads to the idea that the strength of the ph-VF scattering depends on $T_K$. Based on this idea, we will propose a phenomenological model as described below.

In order to examine the possibility of the PGEC state, we have calculated the minimum $\kappa_{ph}$, $\kappa_{min}$ for each compound. $\kappa_{min}$ is a lower limit of $\kappa_{ph}$, which was proposed to describe the phonon glassy states in amorphous systems especially at high temperatures. This was applied to judge the degree of the phonon glassy states in rattling systems (Eu$_8$Ga$_{16}$Ge$_{30}$ and CeFe$_4$Sb$_{12}$) and disordered systems (NaCo$_2$O$_4$). In these systems, $\kappa_{ph}$ approaches $\kappa_{min}$ at high temperatures. Provided no distinction is made between the longitudinal and transverse acoustic phonon modes, the phenomenological expression for $\kappa_{min}$ is given by:

$$m_{AV} = \frac{m_{Ce} + m_{Ni} + m_{Sn}}{3},$$

$$\Gamma(X) = \sum_i c_i (m_{Xi} - m_X)^2 / m_X^2,$$

and

$$m_X = \sum_i c_i m_{Xi},$$

TABLE I. Physical properties of CePtSn, CeNiSn, CeRhSb and CeRhAs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$T_K$ (K)</th>
<th>$T^*$ (K)</th>
<th>$n \times 10^{28}$ (m$^{-3}$)</th>
<th>$\Theta_D$ (K)</th>
<th>$v_{ph}$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CePtSn</td>
<td>7.463$^a$</td>
<td>4.628$^a$</td>
<td>8.016$^a$</td>
<td>10</td>
<td></td>
<td>188</td>
<td>1798</td>
<td></td>
</tr>
<tr>
<td>CeNiSn</td>
<td>7.540$^b$</td>
<td>4.600$^b$</td>
<td>7.614$^b$</td>
<td>51$^c$</td>
<td>15</td>
<td>4.54</td>
<td>228</td>
<td>2147</td>
</tr>
<tr>
<td>CeRhSb</td>
<td>7.415$^d$</td>
<td>4.619$^d$</td>
<td>7.857$^d$</td>
<td>89$^d$</td>
<td>20</td>
<td>4.46</td>
<td>275</td>
<td>2606</td>
</tr>
<tr>
<td>CeRhAs</td>
<td>7.535$^d$</td>
<td>4.308$^d$</td>
<td>7.365$^d$</td>
<td>1350</td>
<td>370</td>
<td>5.02</td>
<td>306</td>
<td>2787</td>
</tr>
</tbody>
</table>

$^a$See Ref. 8.
$^b$See Ref. 10.
$^c$See Ref. 11.
$^d$See Ref. 41.
\[ \kappa_{\text{min}} = \left( \frac{3n}{4\pi} \right)^{1/3} \frac{k_B T^2}{h} \Theta_D \int_0^{\Theta_D / T} x^3 e^{x} \left( e^x - 1 \right)^2 dx, \]

where \( x \) is a dimensionless parameter, \( x = \hbar \omega / k_B T \). The \( \Theta_D \) values of CePtSn and CeRhAs are tentatively calculated by the relation

\[ \Theta_D \approx 1/\sqrt{M \bar{\gamma}}, \]

where \( M \) is the molecular weight, from those of CeNiSn and CeRhSb, respectively, and are tabulated in Table I. The respective \( \kappa_{\text{min}} \)'s calculated by Eq. (5) are plotted in Fig. 3. The \( \kappa_{\text{min}} \)'s of CePtSn, CeNiSn, and CeRhSb are an order of magnitude smaller than \( \kappa_{\text{ph}} \)'s of these compounds at high temperatures. Thus, the PGE\( \overset{\text{C}}{\text{E}} \) state is not realized in the present Ce compounds.

It is interesting to compare the experimental results of \( \kappa_{\text{ph}}(T) \) with the representative T-power dependence, i.e., \( T^2 \) and \( T^{-1} \) as depicted in Fig. 3 at low and high temperatures, respectively. At low temperatures, \( \kappa_{\text{ph}}(T) \) of CeNiSn and CeRhSb follows nearly a \( T^2 \) dependence. An exact \( T^2 \) dependence was observed in CeNiSn only below 2 K, where the el-ph scattering becomes dominant in the presence of \( D_{\text{el}}(E_F) \). At high temperatures, \( \kappa_{\text{ph}} \) of CeRhSb follows approximately the \( T^{-1} \) dependence between 40 K and 140 K. The \( T^{-1} \) dependence means that the ph-ph scattering is dominant. The development of the pseudogap in the electronic density of states would reduce the el-ph scattering so that the phonon mfp associated with the el-ph scattering (pmf\( _{\text{el-ph}} \)) becomes longer than that determined by the ph-ph one (pmf\( _{\text{ph-ph}} \)) in this temperature range.

We propose a phenomenological model to explain the unusual behavior of \( \kappa_{\text{ph}}(T) \) by taking account of ph-VF scattering. At the first step, the effect of the pseudogap formation is neglected. Let us use conventional formula for \( \kappa_{\text{ph}} \) given by the Debye model:

\[ \kappa_{\text{ph}} = \frac{k_B}{2 \pi^2 v_{\text{ph}}} \left( \frac{k_B}{e} \right)^3 T^3 \int_0^{\Theta_D / T} x^4 e^x \tau(x, T) dx. \]

where \( \tau(x, T) \) is the phonon relaxation time. All employed parameters in the calculation of \( \kappa_{\text{ph}} \) are listed in Table I. We consider four processes of phonon scattering as follows:

\[ \tau^{-1} = AT^3 x^2 \exp \left( - \frac{\Theta_D}{2T} \right) + B + C T x + D x^4 T^4. \]

The first term represents the umklapp ph-ph scattering, the second one boundary scattering, the third one the el-ph scattering, and the fourth one the point defect scattering involving the isotope effect as discussed above. In CePtSn, magnons may also carry heat and crystalline-electric-field effects also affect \( \kappa_{\text{ph}} \), but they are tentatively ignored. In VF compounds, it is well known that the el-ph interaction is very strong. The term proportional to \( T_x \) in Eq. (7) was invoked to explain why the \( \kappa \) value of a heavy-fermion compound is lower than that of the La counterpart. A strong hybridization between f electrons of Ce ions and conduction electrons occurs in VF compounds. This indicates that the el-ph interaction of the VF state retains the nature of the conduction electrons and allows one to assume that the ph-VF scattering is equivalent to the el-ph scattering as the first approximation. It should be noted that the el-ph scattering rate in VF compounds described in Ref. 5 is identical to the general expression for the el-ph scattering, \( (m^*)^2 U_{\text{eff}}^2 / 2 \pi \), where \( m^* \) is the effective electron mass, \( U_{\text{eff}} \) the deformation potential, and \( D_m \) the material density. The term \( T_x \) is generally dominant at low temperatures and causes a \( T^2 \) dependence of \( \kappa_{\text{ph}} \). Therefore the enhancement of this term would depress the broad maximum observed in \( \kappa_{\text{ph}} \) around 40 K, and moreover, it should be also responsible for the reduction of \( \kappa_{\text{ph}} \) above 100 K (see Fig. 3). These considerations suggest that the ph-VF scattering rate is proportional to \( T_x \), and the coefficient \( C \) increases with increasing \( T_K \). The fitted results, keeping this assumption in mind, are given in Fig. 4(a); and the obtained parameters are listed in Table II. For CePtSn, CeNiSn, and CeRhSb, the broad maxima are well reproduced. Since the pronounced enhancement of \( \kappa_{\text{ph}} \) of CeRhAs below \( T_3 = 165 \) K obscures the fitting, we have adjusted the \( \kappa_{\text{ph}} \) value at \( T_3 \). It should be noted again that the lattice modulation in CeRhAs affects \( \kappa_{\text{ph}}(T) \).

In Table II, the ratios \( T_K / C \) are the same order of magnitude for the four compounds, implying that \( C \) is roughly proportional to \( T_K \). Thus, the reduction of \( \kappa_{\text{ph}} \) by the ph-VF
scattering is confirmed. This result would be consistent with an experimental observation of the pronounced softening in acoustic phonon branches of a typical VF compound CeNi compared to those of the La counterpart. The softening of acoustic phonon branches in CeNi means a small gradient in the dispersion curve. Therefore the group velocity of acoustic phonons becomes slower, and thus \( \kappa_{ph} \) would be reduced. The extremely huge \( C \) value of CeRhAs may be consistent not only with the high \( T_K \) but also with a strong el-ph coupling, leading to the observed lattice modulation. Equation (6) could not reproduce the upturn of \( \kappa_{ph} \)'s of all compounds above 100 K. This may be due to the uncertainty stemming from the rather small difference between \( \kappa_{ph} \) and \( \kappa_{el} \) above 100 K and/or the negligence of the detailed phonon frequency spectrum. We note here that similar upturns in \( \kappa_{ph} \) were observed in several Ce-based VF compounds.

IV. SUMMARY

We have performed measurements of the thermal conductivity for isostructural compounds CePtSn, CeNiSn, CeRhSb, and CeRhAs with \( e \)-TiNiSi-type structure in order to study the effects of both the VF and the pseudogap formation on \( \kappa_{ph} \). In this series of compounds with no atomic disorder, the phonon-scattering processes, except the ph-VF one, are expected to be almost the same. Furthermore, \( \kappa_{ph} \) is much larger than \( \kappa_{el} \), especially below 100 K. It is noteworthy that these facts assure us of the systematic and precise discussion about the effects of the VF and the pseudogap formation on \( \kappa_{ph} \). In fact, it is evidenced that \( \kappa_{ph} \) is progressively reduced with increasing \( T_K \) due to the enhancement of the ph-VF scattering rate. This assertion may be concluded for CeRhAs above \( T_3 \), but the effect of the lattice modulation cannot be neglected. A PGEC state is not realized in all these compounds. The enhancement of \( \kappa_{ph} \) due to the pseudogap formation is also manifested in this study. In CeRhAs with \( T^* = 370 \) K, the pronounced enhancement of \( \kappa_{ph} \) is observed. On the other hand, the smaller enhancement of \( \kappa_{ph} \) occurs in CeNiSn or CeRhSb with \( T^* \) of 15–20 K. Such a different behavior may originate from the competition between the pmfp(\( el-ph \)) and the pmfp(\( ph-ph \)), i.e., pmfp(\( el-ph \)) < pmfp(\( ph-ph \)) in CeRhAs, and pmfp(\( ph-ph \)) < pmfp(\( el-ph \)) in CeNiSn or CeRhSb below \( T^* \), respectively. The research on the significant reduction of \( \kappa_{ph} \) by the ph-VF scattering has only just begun, and this study is expected to serve as one of the clues in searching for novel thermoelectric materials with low thermal conductivity.

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