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## The anomalous valence state of Eu and magnetic order in $\text{EuRh}_2\text{P}_2$

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**Abstract.** According to  $L_{\text{III}}$  x-ray absorption, Mössbauer effect measurements, lattice constants and static susceptibility, Eu in the novel compound  $\text{EuRh}_2\text{P}_2$  is non-integral valent with a valence of the order of 2.2. On the other hand, the compound orders antiferromagnetically below 50 K, the  $^{151}\text{Eu}$  Mössbauer isomer shift is rather independent of temperature, and the resistivity shows no anomalies in the paramagnetic region. Hence, according to existing theories the Eu 4f level cannot be strongly hybridized with the conduction band as in usual intermediate-valent compounds. We therefore propose a considerable participation of the 4f electrons in a covalent Eu–P bond. However, the absence of the ESR signal of  $\text{EuRh}_2\text{P}_2$  as well as the small but finite temperature dependence of the  $L_{\text{III}}$  valence clearly demonstrate that the hybridization of the 4f electrons with the conduction band is not negligible in this compound.

Because of the small extent of the 4f shell in rare-earth (RE) atoms it is generally assumed that the 4f electrons do not participate significantly in bonds with neighbouring atoms. The number of electrons in the 4f shell (then corresponding to valency and ionicity [1]) is integral and the 4f shell retains its atomic character, i.e. the electrons are arranged according to Hund's rules.

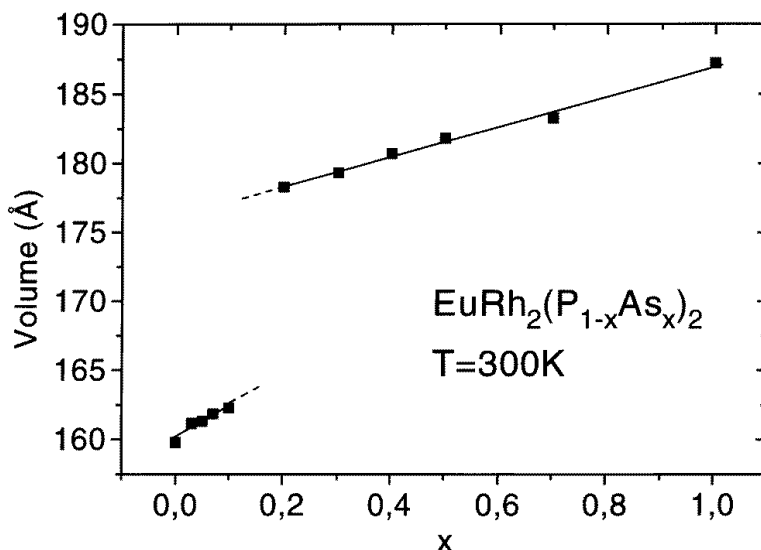
In intermediate-valent compounds like, e.g.,  $\text{EuCu}_2\text{Si}_2$ , the 4f level is pinned to the Fermi energy, and a 4f electron switches between the localized 4f state and the completely delocalized conduction band [2]. This leads to strong anomalies in many physical properties [3], among them the resistivity [4]. Nevertheless, at any given moment the above-discussed concept of integer valences holds, and the valence is non-integral only averaged over time. The time-scale for the fluctuation is  $10^{-11}$  to  $10^{-13}$  s, corresponding to a lifetime broadening of the 4f level of 1 to 100 meV, as can be measured using quasielastic neutron scattering [5]. Because the lifetime broadening is larger than the Zeeman splitting of the levels of the magnetic ion, the  $J_z$ -levels are equally populated and no magnetic ordering occurs [6]. Instead, at low temperatures the susceptibility saturates at a finite value.

Apart from the trivial case of a static mixture of different-valent RE atoms, there are only a few clear-cut exceptions from this general picture: in  $\text{YbPd}$  and  $\text{Yb}_3\text{Pd}_4$  with decreasing temperature the linewidth gets smaller than the ordering temperature [7]. Then the compound has to be regarded as a nearly static mixture in this temperature range and can order magnetically. A decreasing quasielastic linewidth was also observed in intermediate-valent  $\text{TmSe}$ , that orders at 3.3 K [8]. However, it is important that in this case both  $\text{Tm}^{2+}$

and  $\text{Tm}^{3+}$  possess a magnetic moment, while in most other RE only one configuration, e.g.  $\text{Eu}^{2+}$ , is magnetic.

The coexistence of intermediate valency and magnetic order has been supposed to explain the properties of  $\text{Eu}(\text{Pd}_{1-x}\text{Au}_x)_2\text{Si}_2$  with  $0.175 < x \leq 0.3$  at high pressure [9, 10]. From the pressure dependencies of the magnetic hyperfine field and isomer shift in Mössbauer effect measurements on samples with  $x = 0.2$  and  $0.3$  it was concluded that magnetic ordering with an enhanced hyperfine field occurs up to  $p < 2.1$ , but vanishes rapidly with increasing valence [10]. However, it is important to mention that the stoichiometry of the samples investigated is close to that of strongly intermediate-valent  $\text{EuPd}_2\text{Si}_2$  and that the above conclusions were drawn from average values, because the Eu atoms in the alloy series are of course not equivalent due to a random distribution of the Pd/Au atoms.

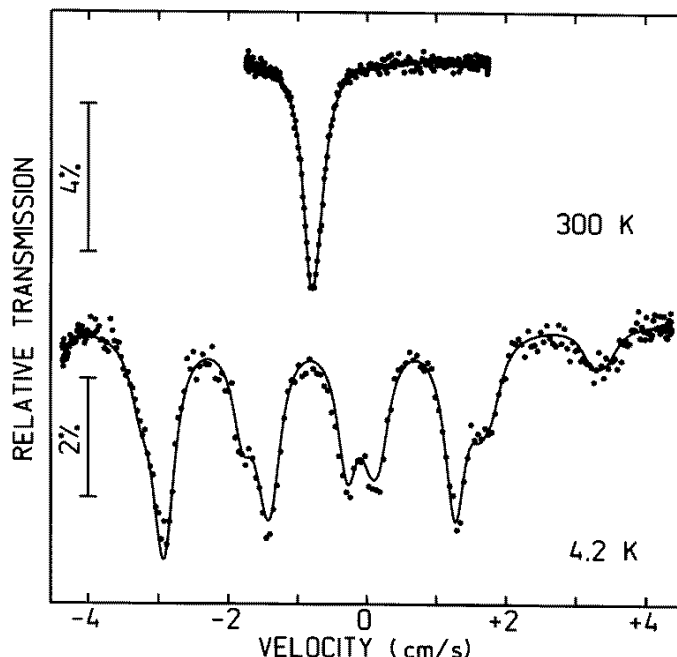
In this paper we show that  $\text{EuRh}_2\text{P}_2$  is a magnetically ordering compound with equivalent Eu atoms, that is non-integral valent according to measurements of the lattice constants, Mössbauer isomer shift,  $L_{\text{III}}$  x-ray absorption, static magnetic susceptibility and ESR. We propose that the valence of the order of 2.2 is mainly due to a significant participation of the 4f electrons in the Eu–P binding, but also due to a weak hybridization of this mixed state with the conduction band.



**Figure 1.** The unit cell volume of the  $\text{EuRh}_2(\text{P}_{1-x}\text{As}_x)_2$  compounds as a function of the As concentration  $x$ .

The novel compound  $\text{EuRh}_2\text{P}_2$  crystallizes in the  $\text{ThCr}_2\text{Si}_2$  structure with lattice constants  $a = 4.013 \text{ \AA}$ ,  $c = 9.921 \text{ \AA}$  and a phosphorus position  $z(\text{P}) = 0.3841$  [11]. This leads to a Eu–P distance of  $3.062 \text{ \AA}$ , which is significantly smaller than that found in other isostructural divalent phosphides ( $d_{\text{Eu-P}} \geq 3.125 \text{ \AA}$  [12]) giving a first hint of the non-integral Eu valency in this compound. Unfortunately, the other  $\text{RERh}_2\text{P}_2$  compounds ( $\text{RE} = \text{La-Nd}$ ) do not crystallize in the  $\text{ThCr}_2\text{Si}_2$  structure [13]. Therefore the usual estimation of the valence using an Iandelli plot is impossible for  $\text{EuRh}_2\text{P}_2$ . Nevertheless a clear anomaly of the unit cell volume is found by considering the isostructural alloy series  $\text{EuRh}_2(\text{P}_{1-x}\text{As}_x)_2$  giving further evidence for non-integral Eu valency in  $\text{EuRh}_2\text{P}_2$ .

As shown in figure 1 the volume smoothly decreases with decreasing  $x$  between  $x = 1$  and  $x = 0.2$ . At this concentration a collapse of about 9% occurs. This anomalous concentration dependence of the unit cell volume indicates a smaller Eu ionic radius (i.e. higher valence) in  $\text{EuRh}_2\text{P}_2$  than in  $\text{EuRh}_2(\text{P}_{1-x}\text{As}_x)_2$  with  $x \geq 0.2$ . Note that a volume anomaly of about 10% corresponds to a valence difference of about 0.23 between (divalent)  $\text{EuRh}_2\text{As}_2$  and  $\text{EuRh}_2\text{P}_2$ .

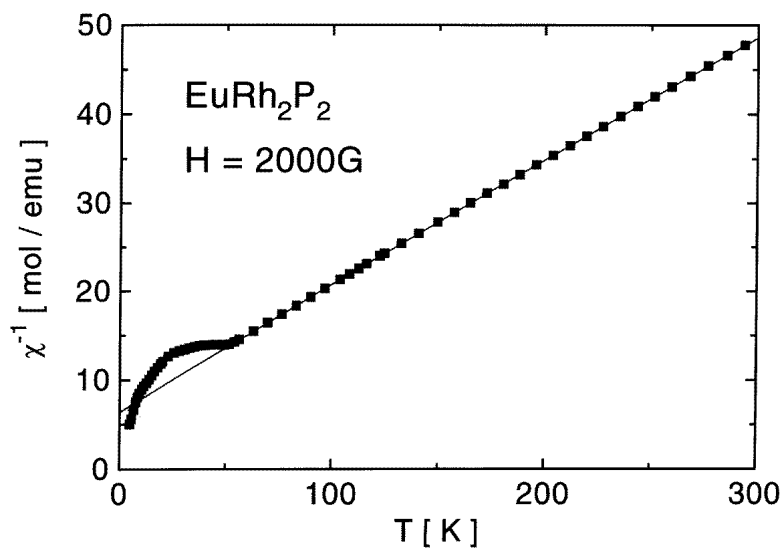


**Figure 2.** Mössbauer spectra of  $\text{EuRh}_2\text{P}_2$  at 300 K and 4.2 K. The solid lines are fits to the data (see the text).

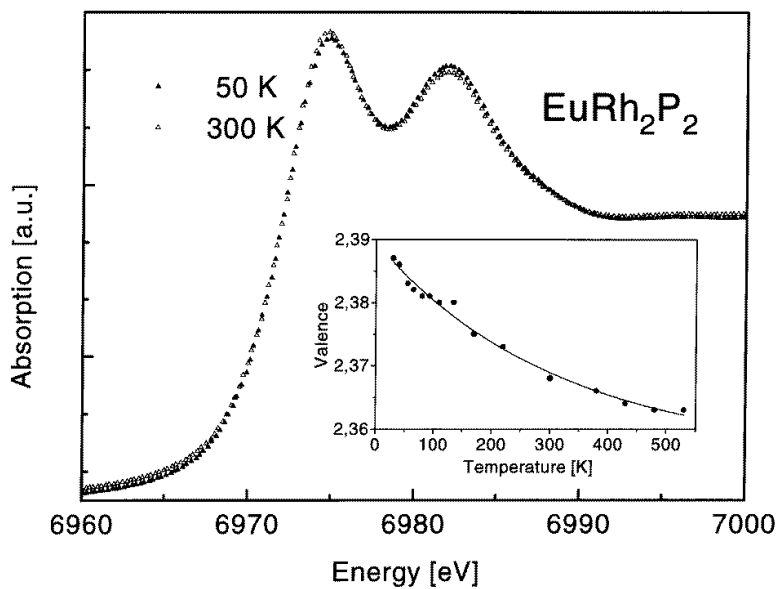
The Mössbauer spectrum at room temperature (figure 2, top) consists of a single line at  $S = -7.78 \text{ mm s}^{-1}$  with a linewidth of  $2.80 \text{ mm s}^{-1}$  corresponding to the natural linewidth. This clearly proves that all Eu atoms are equivalent. The absolute value of  $S$  gives a further indication of non-integral valence of Eu: assuming a difference  $S^{3+} - S^{2+} = 11\text{--}13 \text{ mm s}^{-1}$ , a comparison with the isomer shift  $S = -11.09 \text{ mm s}^{-1}$  of isostructural  $\text{EuRh}_2\text{As}_2$  yields a Eu valence of  $\nu = 2.24\text{--}2.29$  for  $\text{EuRh}_2\text{P}_2$ .

Non-integral valence is also indicated by the paramagnetic static susceptibility. The inverse susceptibility that is shown in figure 3 follows a Curie–Weiss law indicating that the effective magnetic moment (and hence the valence) does not exhibit a strong temperature dependence. However, the effective moment of  $7.35 \mu_B$  is clearly reduced relative to the free- $\text{Eu}^{2+}$  value ( $7.94 \mu_B$ ). In the ionic model the effective moment corresponds to a Eu valence of about 2.15. For comparison,  $\text{EuRh}_2\text{As}_2$  has a magnetic moment of  $7.86 \mu_B$ .

Measurements of the Eu  $L_{\text{III}}$  x-ray absorption were performed at HASYLAB, beamline EXAFS II, and at LURE, Orsay, beamline XAS 2. The spectrum of  $\text{EuRh}_2\text{P}_2$  shows a pronounced double-peak structure that even changes slightly with temperature (figure 4)! From the relative area of the white lines we obtain a continuous valence increase from a



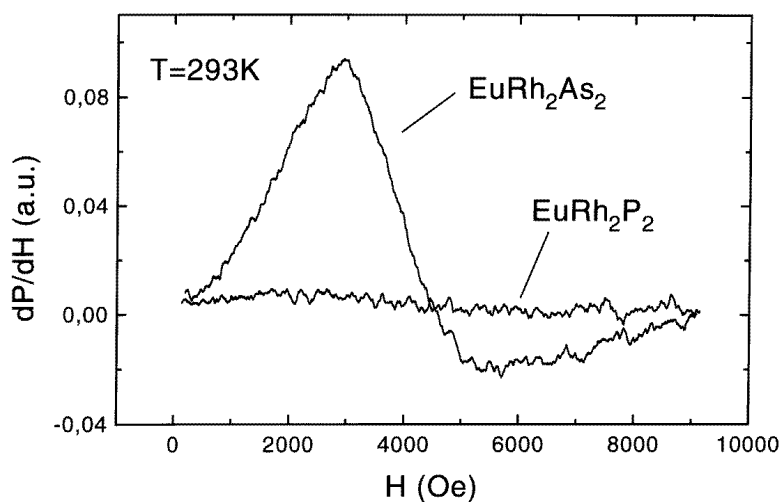
**Figure 3.** The inverse susceptibility of  $\text{EuRh}_2\text{P}_2$ . The straight line corresponds to a Curie-Weiss fit with a Eu moment of  $p_{\text{eff}} = 7.35$ .



**Figure 4.**  $L_{\text{III}}$  x-ray absorption edges of  $\text{EuRh}_2\text{P}_2$  at 50 K and 300 K. Inset: the temperature dependence of the Eu  $L_{\text{III}}$  valence of  $\text{EuRh}_2\text{P}_2$ .

room temperature value of 2.36 to a valence of 2.38 at 30 K. Both the very pronounced double-peak structure and the temperature dependence of the absorption edge are in striking contrast to the observations for compounds with divalent Eu and stable moments. Thus the  $L_{\text{III}}$  spectra of  $\text{EuRh}_2\text{P}_2$  clearly prove an unusual valence state of Eu in this compound.

In contrast to this we observed an  $L_{III}$  spectrum of  $\text{EuRh}_2\text{As}_2$  that was typical for stable divalent Eu compounds.



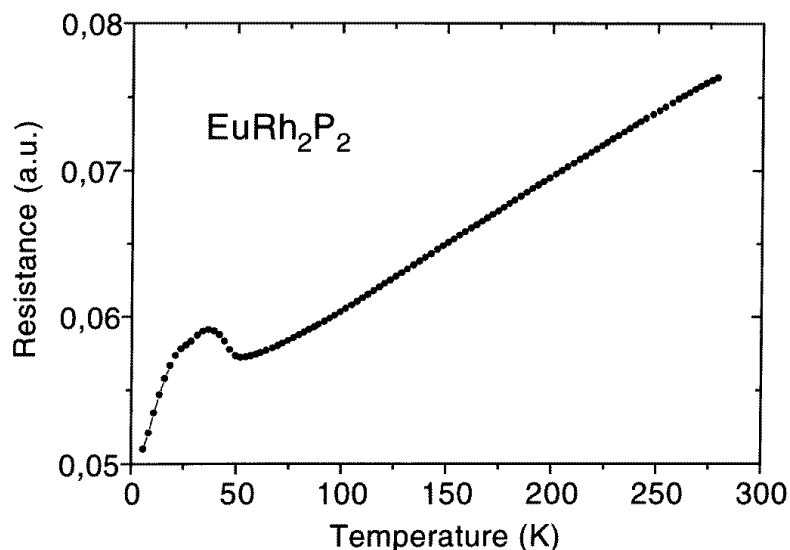
**Figure 5.** ESR spectra of  $\text{EuRh}_2\text{P}_2$  and  $\text{EuRh}_2\text{As}_2$  at 293 K.

ESR measurements were made on  $\text{EuRh}_2\text{As}_2$  and  $\text{EuRh}_2\text{P}_2$  at 9.3 GHz (figure 5). Already at room temperature  $\text{EuRh}_2\text{As}_2$  shows a strong signal with a  $g$ -factor  $g = 1.97$ , typical for divalent Eu ions in a metallic host [14]. With decreasing temperature its intensity increases until the ordering temperature is reached. Then the signal strongly shifts towards higher fields out of the field sweep range.

In sharp contrast to that, in  $\text{EuRh}_2\text{P}_2$  the ESR signal above 50 K is practically absent. From a comparison with isostructural  $\text{EuRh}_2\text{As}_2$  one has to conclude that the absence of the bulk ESR signal is caused by the non-integral valency of Eu: even a small broadening of the 4f level due to charge fluctuations leads to disappearance of the ESR signal, if the width of the 4f state exceeds the characteristic energy scale of the measurement (0.04 meV at 10 GHz) [15].

From all of these measurements we can conclude unambiguously that the occupancy of the Eu 4f level in  $\text{EuRh}_2\text{P}_2$  is non-integral, i.e. it is not a pure  $4f^7$  state. Nevertheless the compound orders magnetically: below  $T_N = 50$  K the Mössbauer spectrum is completely split (figure 2, lower panel). At 4.2 K the hyperfine field is 54 T, much larger than the value of about 30 T usually observed for Eu intermetallic compounds, and the quadrupole splitting amounts to  $-3.7 \text{ mm s}^{-1}$ . The isomer shift remains unaffected by the magnetic order. The antiferromagnetic ordering is clearly observable in the magnetic susceptibility, which decreases below 50 K, and the resistivity (figure 6) showing a pronounced anomaly at  $T_N$ .

What is the physical origin of the coexistence of non-integral valency and magnetic order? In a model for intermediate-valent compounds Nolting *et al* (see [16]) showed that an enhanced exchange interaction between localized 4f spins and conduction electron spins may lead to an enhancement of the ordering temperature relative to the stable-valent case. However, if the electronic fluctuations get too strong, the ordering temperature decreases rapidly and vanishes, and this is probably the case for  $\nu \geq 2.2$ .



**Figure 6.** The resistivity of  $\text{EuRh}_2\text{P}_2$  as function of temperature.

In order to explain only weak 4f hybridization, necessary to account for the magnetic order within existing theories, along with the large Eu valence of  $\nu \geq 2.2$ , we propose in addition a significant participation of the Eu 4f electrons in the Eu–P binding either directly or via the Eu 5d–P 2p hybridized states. Such a participation was already indicated by band-structure calculations for  $\text{CeO}_2$  and  $\text{PrO}_2$  [1]. In this scenario the 4f electron is not fully localized at the RE atom; therefore the 4f occupancy is not integer. With this assumption one can explain the reduced Mössbauer isomer shift, the  $L_{\text{III}}$  valence and the reduced unit cell volume, since all of these measurements are only sensitive to the charge screening due to the 4f electrons. This is significantly reduced if the 4f state is hybridized with the phosphorus 2p states. On the other hand, due to the localization of the 4f electron in the Eu–P binding, the information about the spin is mostly preserved. Therefore magnetic ordering via the RKKY exchange interaction is possible here, while it is not possible in the strongly intermediate-valent regime, where the spin information is lost into the conduction band. This scenario is supported by the absence of any anomaly of the resistivity, which shows a very simple linear behaviour in the paramagnetic phase. From this lack of an anomalous behaviour of  $\rho$  we conclude that the lifetime broadening of the 4f level is less than about 4 meV ( $T_N k_B$ ).

However, the absence of an ESR line in  $\text{EuRh}_2\text{P}_2$  cannot be explained by the assumption of a covalent bond alone. Indeed, even in strongly covalent bound states (like, e.g., d-ion–oxygen binding in insulators) the levels remain atomically sharp and an ESR signal is observable. Therefore the absence of an ESR signal shows the broadening of the Eu 4f(5d)–P 2p level with a lower limit for its width of about 0.04 meV (see above). This means that the hybridized state must cross the Fermi level and electrons from this state really go into the conduction band, thus broadening the hybridized state. A weak hybridization with the conduction electrons is not only a conclusive consequence of the missing ESR signal but is also supported by the small, but finite temperature dependence of the  $L_{\text{III}}$  valence. In the model of Nolting the weak hybridization with the conduction band is fully compatible with

the observed magnetic order. It might also be responsible for the extremely large hyperfine field. However, we emphasize that in our opinion the 4f hybridization with the conduction band is not directly related to the observed strong deviations from the Eu 4f<sup>7</sup> state.

The Eu–P bond seems to be susceptible to a participation of the 4f electrons: there are several compounds with Eu embedded in a cage of P, that are non-integral valent according to different measurements but order magnetically: EuPd<sub>2</sub>P<sub>2</sub> crystallizing also in the ThCr<sub>2</sub>Si<sub>2</sub> structure shows a volume anomaly [17] and a trivalent intensity in L<sub>III</sub> x-ray absorption [18] that increases under pressure [19]. On the other hand, the compound orders magnetically, the effective moment is 8  $\mu_B$ , there is a good ESR signal and the Mössbauer isomer shift (−9.73 mm s<sup>−1</sup>) is in the usual range for divalent Eu [17, 18]. Therefore, in this compound covalence effects seem to be present, whereas there is no evidence for any hybridization between 4f and conduction electrons.

EuFe<sub>4</sub>P<sub>12</sub> orders ferromagnetically even at 99 K [20, 21]. Because of the magnetic order the authors claimed the compound to be divalent, although the magnetic moment is strongly reduced (6.2  $\mu_B$ ) and the (temperature-independent) isomer shift (−6.0 mm s<sup>−1</sup>) is between typical divalent and trivalent values. To complete the analogy to EuRh<sub>2</sub>P<sub>2</sub>, the hyperfine field (−67 T) is extremely large, too. In first measurements of the L<sub>III</sub> absorption edge we find an even more pronounced double-peak structure than in EuRh<sub>2</sub>P<sub>2</sub> yielding a valence of about 2.5 at room temperature. Measurements in the near future are planned to study whether these very strange findings for EuFe<sub>4</sub>P<sub>12</sub> are due to covalence effects alone or whether there is in addition a finite hybridization between 4f and conduction electrons similar to that in EuRh<sub>2</sub>P<sub>2</sub>.

To summarize, we have shown that Eu in EuRh<sub>2</sub>P<sub>2</sub> orders magnetically and is non-integral valent. The last point was verified by finding a double-peaked structure in the L<sub>III</sub> x-ray absorption, the <sup>151</sup>Eu isomer shift, a reduced static magnetic moment, a missing ESR signal and an anomalous behaviour of the unit cell volume in the EuRh<sub>2</sub>(P, As)<sub>2</sub> series. Many of the experimental findings can be explained by strong covalence effects. The absence of the ESR signal, however, shows that a finite hybridization with the conduction band is present. In order to investigate this weak 4f hybridization, high-pressure <sup>151</sup>Eu Mössbauer experiments and measurements of the specific heat and transport properties at very low temperatures are intended.

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