Theoretical predictions of superconductivity in alkali metals under high pressure

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We calculated the superconductivity properties of alkali metals under high pressure using the results of band theory and the rigid-muffin-tin theory of Gaspari and Gyorffy. Our results suggest that at high pressures lithium, potassium, rubidium, and cesium would be superconductors with transition temperatures approaching 5–20 K. Our calculations also suggest that sodium would not be a superconductor under high pressure even if compressed to less than half of its equilibrium volume. We found that the compression of the lattice strengthens the electron-phonon coupling through a delicately balanced increase of both the electronic and phononic components of this coupling. This increase of the electron-phonon coupling in Li is due to an enhancement of the *s-p* channel of the interaction, while in the heavier elements the *p-d* channel is the dominant component.

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I. INTRODUCTION

Neaton and Ashcroft[1] predicted that at high pressures Li might be a superconductor either in paired structures or monatomic. Subsequently, Christensen and Novikov[2] showed that fcc Li under increased pressure may reach a superconducting transition temperature $T_c=50-70$ K. This prediction has been supported by Shimizu *et al.*[3] and Struzhkin *et al.*,[4] who reported measurements of superconductivity in compressed Li with a T_c ranging from 9 to 20 K. The overestimate of T_c reported in Ref. 2 is probably due to an error by these authors, as we discuss in Sec. III. Using the rigid-muffin-tin approximation (RMTA) formulated by Gaspari and Gyorffy,[5] we performed calculations for two other alkali metals, K and Rb, and predicted that at high pressures they both would be superconductors with transition temperatures approaching 10 K.[6] Before these works, the only known superconducting alkali metal was Cs, which becomes superconducting above 7.0 GPa with a transition temperature of about 1.5 K.[7] Similar theoretical results for Li, K, and Cs were also reported by Ashcroft,[8] Profeta *et al.*,[9] Kasinathan *et al.*,[10] Tse *et al.*,[11] and Stocks *et al.*[12]

In this paper, we have extended our study to Li, Na, and Cs again using the RMTA. Our calculations demonstrate that Li and Cs display superconductivity at high pressure above 15 and 3.5 GPa, respectively. Our results also showed the lack of superconductivity for Na up to 90 GPa. We compare these new calculations with our previous results of K and Rb to show a complete picture of superconductivity properties of alkali metals under high pressure. Our calculations indicate that the *s-p* channel of contribution to the Hopfield parameter η dominates Li under high pressure, while the *p-d* channel contribution is the major reason that K, Rb, and Cs become superconductors under high pressure.

The massive structural phase transitions of all alkali metals have be extensively investigated during the past few decades.[11,13–19] All alkali metals were found to be stable with bcc structure under ambient pressure and will transform to the fcc structure at about 20, 65, 11.5, 7, and 2.3 GPa pressure for Li, Na, K, Rb, and Cs, respectively. In this paper, our investigations are focused on the bcc and fcc structures within the above pressure ranges which correspond to volume changes as large as 40% of equilibrium. The conclusions we draw in this paper are valid for the structure which is stable in the experimental range of pressure.

Tomita *et al.*[20] recently reported experimental results for Li, Na, and K. They confirmed the superconductivity of Li above 20 GPa at temperatures reaching 15 K. They also pointed out the absence of superconductivity in Na and K for pressure up to 65 and 43.5 GPa, respectively, without specifying whether the measurements were extended to the fcc phase. However, for K, our calculations and those of Profeta *et al.*[9] show superconductivity in the fcc phase. Further experimental work may be required.

II. THEORY AND COMPUTATIONAL DETAILS

McMillan's strong coupling theory[21] defines an electron-phonon coupling constant by

$$\lambda = \frac{\eta}{M\langle\omega^2\rangle} = \frac{N(\epsilon_F)\langle I^2\rangle}{M\langle\omega^2\rangle}, \tag{1}$$

where M is the atomic mass, η is the Hopfield parameter,[22] $N(\epsilon_F)$ is the total density of states (DOS) per spin at the Fermi level, ϵ_F, $\langle I^2\rangle$ is the square of the electron-ion matrix element at ϵ_F, and $\langle\omega\rangle$ is the average phonon frequency. The $\langle I^2\rangle$ is determined by the RMTA approximation given by the Gaspari and Gyorffy[5] (GG) formula,

$$\langle I^2\rangle = \frac{\epsilon_F}{\pi^2}\sum_l 2(l+1)\frac{\sin^2(\delta_{l+1}-\delta_l)}{N_l^{(1)}N_{l+1}^{(1)}}\frac{N_l N_{l+1}}{N^2(\epsilon_F)}, \tag{2}$$

where δ_l are scattering phase shifts, $N_l(\epsilon_F)$ is the lth component of the DOS per spin, and $N_l^{(1)}$ is the free-scatterer DOS.

There are two important papers that address the question of the spherical approximation in the GG theory. The first one by John[23] shows that the GG formula is exact for cubic systems with one atom in the unit cell and with $l+1$ up to 2. This validates our results for Li and Na where the *p-d* and *d-f* channels have negligible contributions. In addition, Butler *et al.*[24] have obtained a generalization of the GG formula

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for $l>2$ that is exact for systems in which all atoms sit at sites having cubic symmetry. Their expression contains certain cross terms which they showed have small or canceling contributions to the value of η. Therefore, our calculations for K, Rb, and Cs which have strong diagonal contributions from p-d but not d-f scattering are also reliable.

In order to determine the quantities entering Eq. (2), we performed augmented plane wave (APW) calculations of the band structures and total energies of the targeted alkali metals in the local density approximation (LDA) following the Hedin-Lundqvist prescription[25] in both bcc and fcc structures, for a wide range of pressures. Since the LDA underestimates the equilibrium lattice constant of alkali metals by approximately 3%, we applied a uniform shift to our results for $E(V)$ so that at the experimental equilibrium volume we have the minimum energy. To accomplish this the pressure shifts are 1.5, 0.4, 0.4, 0.4, and 0.25 GPa for Li, Na, K, Rb, and Cs, respectively. We also used the APW results to determine the pressure variation of the bulk moduli B. The B values were used to compute the average phonon frequency which has been taken to be proportional to the product of bulk modulus and volume,[26]

$$\langle \omega^2 \rangle = CB(V)V^{1/3}, \tag{3}$$

where the constant C is determined by the $\langle \omega^2 \rangle$ and the Debye temperature Θ_D under normal pressure using the formula:

$$\omega^2 = \frac{1}{2}\Theta_D^2. \tag{4}$$

The approximation made in using Eq. (3) and Eq. (4) gives reasonable values of λ and leads us to believe that our results should differ only quantitatively from direct phonon evaluations via linear response theories. The transition temperature for superconductivity is given by the McMillan equation,[21]

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \tag{5}$$

where μ^* is the Coulomb pseudopotential, which we have set equal to 0.13.

III. RESULTS

Before we present our detailed results, we wish to bring to the attention of the reader that in our opinion there must be an error in the evaluation of η for Li by Christensen and Novikov.[2] The error is that in Eq. (1) they must have used $N(\epsilon_F)$ for two spins instead of one as is the correct implementation of the McMillan theory. Figure 1 (left panel) demonstrates a clear discrepancy between our results and those of Ref. 2. Dividing the η of Ref. 2 by 2 gives a perfect agreement with our results as shown in Fig. 1 (right panel) and as we discuss below lowers the value of λ and brings T_c close to the measured value.

To demonstrate the effect of high pressures on the density of states at the Fermi level for alkali metals, we plotted the total density of states and its angular momentum decompositions for fcc Li and Cs under ambient and high pressures (41 GPa for Li and 3.6 GPa for Cs)[27] in Fig. 2. For Li, we note that both $N(\epsilon_F)$ and its angular momentum decompositions decrease under pressure. On the other hand, for Cs we observe a decrease of the s- and p-like density of states with a remarkable increase of the d-like density of states $N_d(\epsilon_F)$ under high pressure. This increase of the d density of states at ϵ_F makes the largest contribution to the large value of η at large pressure as discussed below. We also observed the same trend as in Cs for the alkali metals K and Rb. In contrast, for both the bcc and fcc phases of Li and Na, the density of states decreases as the lattice is compressed. This fact gives a partial explanation of the absence of superconductivity under high pressure for Na. For Li, however, the

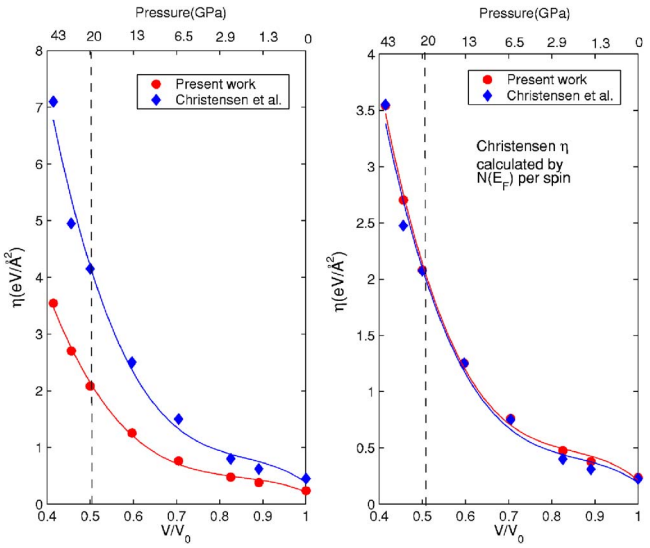

FIG. 1. (Color online) Comparison of η between our results and Christensen and Novikov for fcc Li in the left panel, and the corrected result in the right panel. The vertical dashed line indicates the transition from bcc to fcc.

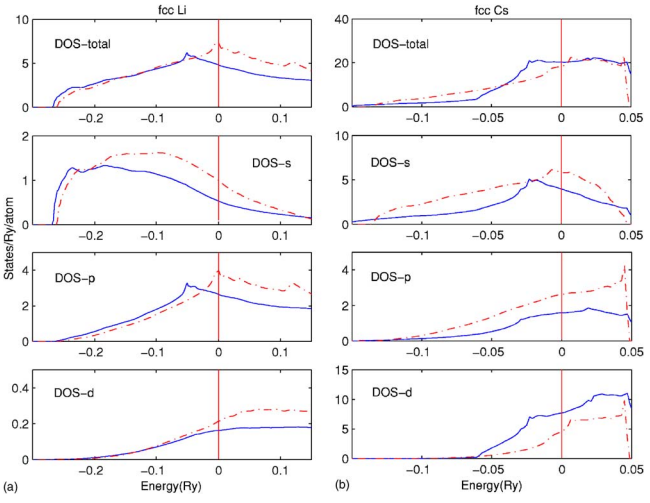

FIG. 2. (Color online) Total density of states and angular momentum decompositions of fcc Li and Cs under normal and high pressure. The solid and dashed lines denote the high and ambient pressure, respectively.

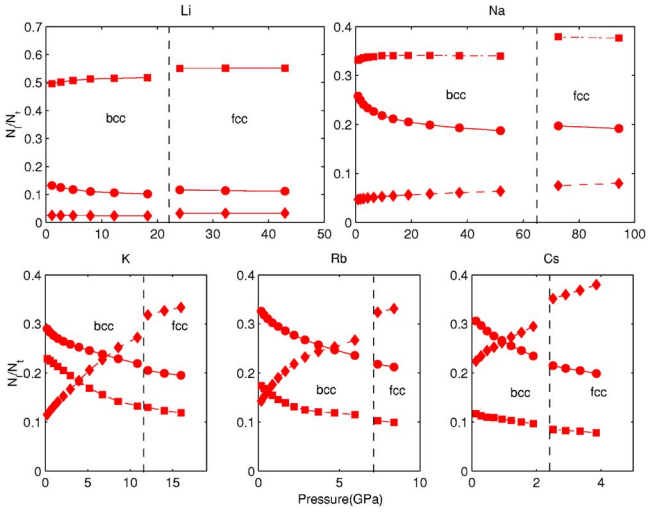

FIG. 3. (Color online) Angular momentum decomposed DOS divided by the total DOS at ϵ_F, the filled square; circle and diamond symbols denote s, p, and d states, respectively.

increase in the matrix element $\langle I^2 \rangle$ is strong enough to ensure the overall large increase in η, which we will discuss later.

We show the ratios $N_l(\epsilon_F)/N(\epsilon_F)$ as a function of pressure in Fig. 3, where the vertical line indicates the pressure where the transition from bcc to fcc occurs in the experiments. These ratios are crucial in the determination of η. It is important to note that the ratio $N_d(\epsilon_F)/N(\epsilon_F)$ of the heavier alkali metals K, Rb, and Cs increases rapidly as a function of increasing pressure. The buildup of the d-like DOS under high pressure causes the large values of η for the heavier elements under high pressure shown in Fig. 4. For Li and Na, the d ratio is very small and the s ratio dominates. We note that for Na, the p ratio decrease with increasing pressure.

In Fig. 4, we show the total η and its contributions from s-p, p-d, and d-f scattering channels as a function of pressure in both the bcc and fcc structures. Total η in all five

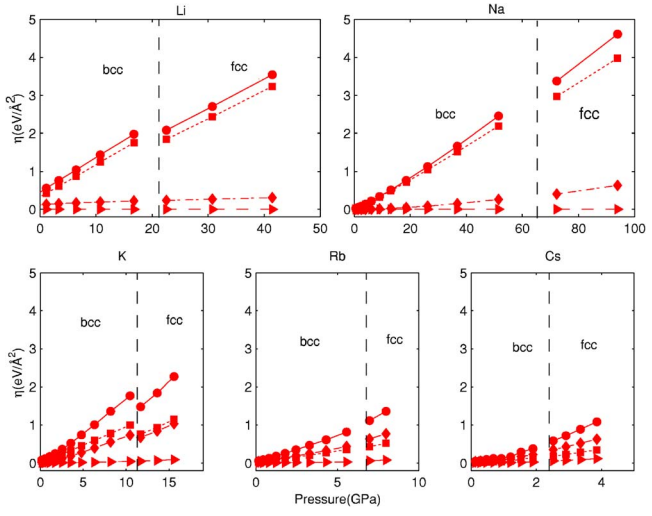

FIG. 4. (Color online) Total η and its contributions from the s-p, p-d, and d-f channels; the filled circle, square, diamond, and triangle symbols denote total, s-p, p-d, and d-f channels, respectively.

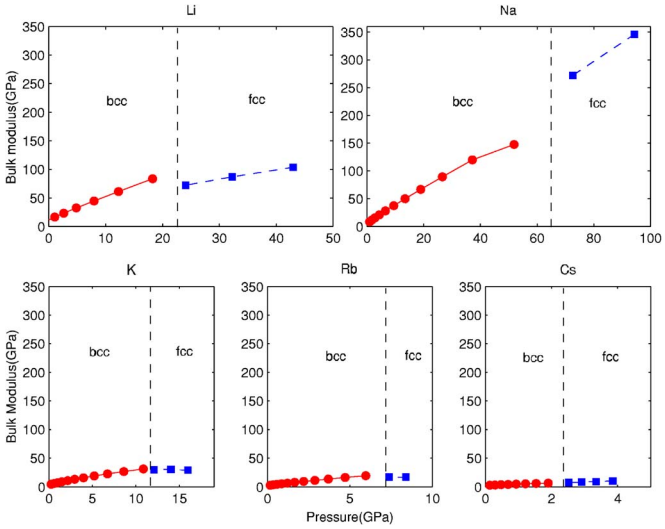

FIG. 5. (Color online) The bulk moduli B as a function of pressure; the filled circle and square symbols denote bcc and fcc, respectively.

alkali metals in the bcc and fcc lattices increases significantly with increasing pressure. Among all alkali metals, Li has the second largest increase of η with increasing pressure, which is one of the reasons why Li is a superconductor under high pressure. Figure 4 shows that different elements have different scattering channels as the dominant contributors to the total η. More specifically for Li and Na, the η contribution of the s-p channel increases rapidly with increasing pressure while the other two contributions remain around zero. For K and Rb, when pressure is increased the η contributions from both the s-p and p-d channels increase quickly. For Cs, the p-d channel contributes the major increase of η with pressure increasing. For all elements, the η contribution of d-f channel is always very close to zero. The graph also demonstrates that the largest portion of the η increase in Li and Na under high pressure is contributed by the s-p channel. Na shows the largest value of η among all the alkali metals when pressure reaches 90 GPa. However, as we discuss below, Na has a very large value of $\langle \omega \rangle$ which lowers the value of λ significantly.

Figure 5 shows the increase of the bulk modulus B as a function of pressure. We note that the bulk moduli of Li and Na increase dramatically with increasing pressure. The bulk modulus increase of K, Rb, and Cs is around 1/3 to 1/10 of that for Li and Na. Figure 6 shows the prefactor, $\langle \omega \rangle$, in the McMillan equation. We note that the $\langle \omega \rangle$ for Li and Na, in both bcc and fcc structures, increases much faster than in the other alkali metals. This is the other reason that Li has larger T_c than K, Rb, and Cs despite the fact that λ of K, Rb, and Cs can be larger than that of Li under pressure. Combining the values of η and $M\langle \omega^2 \rangle$, we determined the electron-phonon coupling constant λ using Eq. (1). In Fig. 7, we show λ as a function of pressure. It is evident that for the alkali metals Li, K, Rb, and Cs, under pressure λ reaches large values, suggesting that these metals could display superconductivity. To quantify our predictions for superconductivity, we have calculated T_c for all five elements in both the bcc

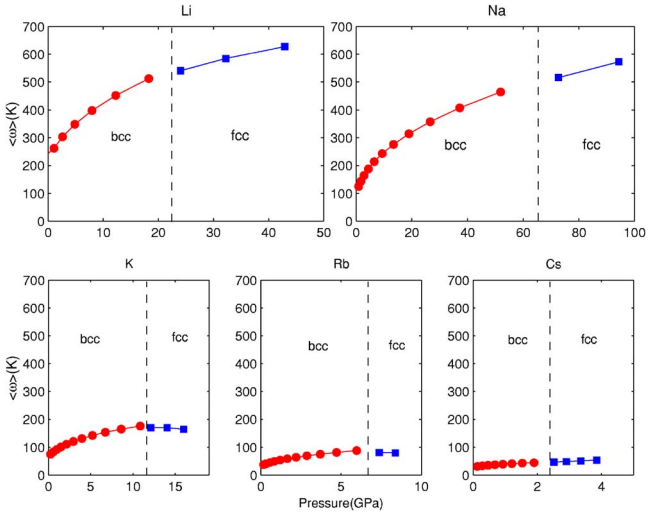

FIG. 6. (Color online) Average phonon frequency $\langle\omega\rangle$ as a function of pressure. The filled circle and square symbols denote bcc and fcc, respectively.

and fcc structures at high pressure using the McMillan equation with Coulomb pseudopotential values $\mu^*=0.13$ and 0.20. Figure 8 shows the T_c of the five alkali metals in the fcc structure as a function of pressure. As one might expect from the large values of the electron-phonon interaction λ, the elements Li, K, Rb, and Cs are predicted to be superconductors with T_c larger than 5 K for pressures higher than 20, 11, 7, and 3.5 GPa, respectively. Clearly our results for the value of T_c are sensitive to the value of μ^* and increase of μ^* to 0.2 suppresses T_c by a factor of 4 for Li and about 20% to 40% for K, Rb, and Cs, as shown in Fig. 8.

Our calculations suggest that Na does not display superconductivity because the electron-phonon coupling constant λ remains small ($\lambda \approx 0.25$) for compressions up to 90 GPa as shown in Fig. 7. The absence of superconductivity for Na is

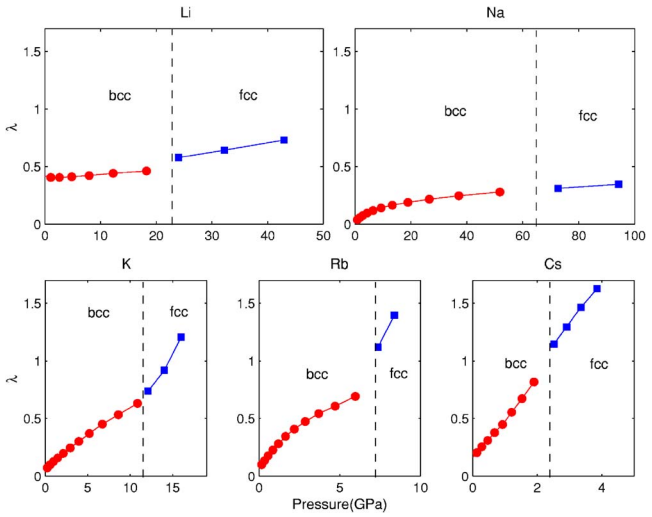

FIG. 7. (Color online) Electron-phonon coupling constant λ as a function of pressure. The filled circle and square symbols denote bcc and fcc, respectively.

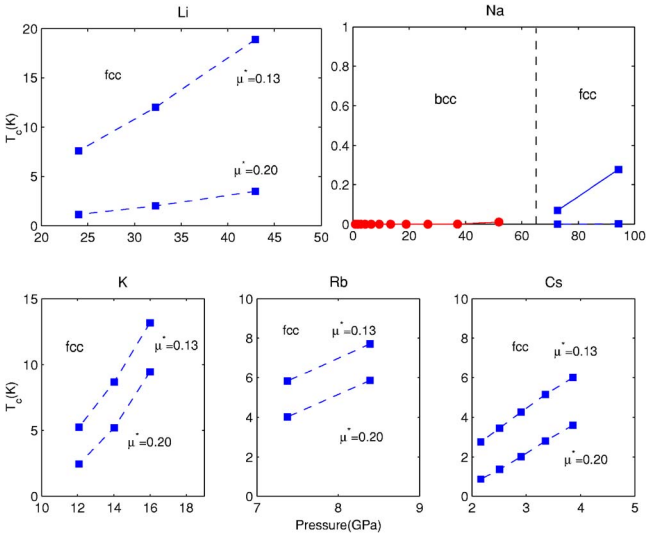

FIG. 8. (Color online) Transition temperature T_c as a function of pressure; the filled circle and square symbols denote bcc and fcc, respectively.

determined by a delicate balance of the increasing electronic and phononic components of the electron-phonon coupling constant. Na has an η which increases faster than in K, Rb, and Cs, but slower than in Li. However, the increase of η in Na is mostly canceled out by its $M\langle\omega^2\rangle$, which increases much more rapidly than in K, Rb, and Cs. Therefore, Na does not display strong enough electron-phonon coupling to become a superconductor under high pressure up to 90 GPa in both the bcc and fcc structures. Recent calculations by Cohen *et al.*[28] suggest that for even higher pressures Na might become a superconductor.

IV. CONCLUSIONS

As it can be seen from Eq. (1), the increase of λ may be caused by either an increase of η or a decrease of $M\langle\omega^2\rangle$, or a combination of these two factors. For K, Rb, and Cs, because the increase of the bulk modulus under pressure is slow, the increase of η, which is mainly caused by an increase of $N(\epsilon_F)$, dominates the determination of λ. Therefore, K, Rb, and Cs have a large λ under high pressure, which results in the prediction of superconductivity. The increase of λ in Li under pressure is due to the increase of $\langle I^2\rangle$ rather than $N(\epsilon_F)$, which is actually decreasing under pressure, and overcomes the increase of $M\langle\omega^2\rangle$ which in fact helps by increasing the prefactor $\langle\omega\rangle$ in the T_c equation. Therefore, Li would be a superconductor under high pressure. Na is different from Li and from the other alkali metals because its large η is canceled by the increasing bulk modulus under pressure which reduces the value of λ. Therefore, a delicate balance of η and $M\langle\omega^2\rangle$ results in Li being a superconductor but not Na. Our calculated T_c for Li shown in Fig. 8 is in very good agreement with experiment.[3]

It should be mentioned here that Tse *et al.*[11] argued that the softening of the *TA* phonon branch near the *X* point

causes the occurrence of superconductivity in Li. Our view is that this is an oversimplification and is not a sufficiently quantitative explanation. On the other hand the RMTA takes an average in all directions on the Fermi surface and not just in one high-symmetry point. Regarding the mechanism of superconductivity in K, Rb, and Cs, we suggest that this is due to the increased *d*-like character of the wave functions at ϵ_F at high pressures. This enhanced *d* character near ϵ_F has also been documented by other authors.[29] We used it here to justify the RMTA which is successful in transition metals as shown by Papaconstantopoulos *et al.*[30]

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