

Predicted superconductivity above 100 K in electride Li_4Rh under high pressure

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Although numerous high-pressure electride (HPE) superconductors have been reported, their superconducting transition temperatures (T_c) are low. No HPE superconductor with a T_c exceeding 100 K has been reported. Herein, we predicted a HPE superconductor, Li_4Rh , with a high $T_c = 108.2$ K at 300 GPa, making it the first HPE superconductor with a T_c exceeding 100 K. Li_4Rh features strong hybridization between nonnuclear attractors (NNAs) and atoms near the Fermi level and a large, deformed cylindrical Fermi sheet. This Fermi sheet structure induces strong electron-phonon coupling (EPC) and allows a broad range of electrons and phonons with a wide range of q vectors to participate in EPC, resulting in high T_c . Unlike other HPE superconductors, the T_c of Li_4Rh does not decrease with decreasing EPC but remains stable because the logarithmic average phonon frequency increases as the EPC strength decreases. This helps maintain T_c with increasing pressure with little fluctuation. The results indicate that HPEs with strong hybridization between NNAs and atoms near the Fermi level and with large and closed Fermi surfaces are more likely to exhibit high T_c , offering deep insights into HPE superconductivity and providing valuable guidance for future research into high- T_c electrides.

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Since the discovery of the first superconductor, mercury, researchers have not stopped working to discover high-temperature superconductors [1–3]. Recently, research has shifted toward high-pressure hydrogen-based superconductors, where phonon-mediated Bardeen-Cooper-Schrieffer superconductivity plays a crucial role. These materials exhibit high superconducting transition temperatures (T_c) and have the potential to achieve superconductivity close to room temperature [4–7]. Recently, the discovery of the binary lithium-rich high-pressure electride (HPE) $\text{C2}/c\text{-Li}_6\text{P}$, which has a superconducting T_c of 39.3 K at 270 GPa, has opened exciting new avenues for exploring high-temperature superconductors in HPEs and has attracted significant attention [8]. HPE superconductors represent a novel category of superconductors that are distinct from the well-known conventional high-pressure hydrogen-based superconductors. In high-pressure hydrogen-based superconductors, increasing the hydrogen density of states at the Fermi level is crucial for enhancing electron-phonon coupling (EPC) [9,10]. The recently discovered cagelike hydrogen-based superconductors can improve the hydrogen density of states at the Fermi level by forming high-symmetry hydrogen cages, thereby increasing EPC [4–7]. However, in HPE superconductors, the

electron density of states at the Fermi level is primarily determined by nonnuclear interstitial electrons. High pressure causes valence electrons to detach from atoms and occupy interstitial sites, forming nonnuclear interstitial electrons, which serve as non-nuclear attractors (NNAs) [11]. Therefore, effectively tuning the electronic and dynamic behavior of these NNAs is crucial for adjusting EPC in HPE superconductors [12–15].

Recently, binary lithium-rich HPE superconductors have garnered significant attention because of their diverse NNA topologies and high superconducting T_c values [16–18]. Most studies on binary lithium-rich HPE superconductors have explored their superconductivity primarily through lattice dynamic behaviors and the characteristics of NNAs. For example, in $\text{C2}/c\text{-Li}_6\text{P}$, dumbbell-like NNAs play a dominant role in superconductivity, and low-frequency phonon modes below 10 THz contribute 52.4% to the EPC at 270 GPa [8]. In $\text{C2}/m\text{-Li}_6\text{Al}$, which has shell-like NNAs and a superconducting T_c of 29.0 K at 150 GPa, low-frequency phonon modes below 300 cm^{-1} account for approximately 59.0% of the EPC [16]. However, in some high- T_c HPE superconductors, medium-frequency phonon modes have been shown to be more influential in EPC. For example, $\text{Fm}\bar{3}m\text{-Li}_8\text{Au}$, which features isolated octahedronlike NNAs, has the highest T_c of 73.1 K at 250 GPa among HPE superconductors, with medium-frequency phonon modes contributing to 50.8% of the EPC [17]. In contrast, in $\text{C2}/c\text{-Li}_6\text{As}$, which are isostructural to $\text{C2}/c\text{-Li}_6\text{P}$ and exhibit a T_c of 45.2 K at 270 GPa, low-, medium-, and high-frequency phonon modes have almost equal contributions to EPC [12]. Overall, although phonon modes at different frequencies affect different HPE superconductors in unique ways, all HPE superconductors share

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a common feature: the T_c increases with increasing EPC strength (λ), whereas changes in T_c are inversely related to variations in the logarithmic average phonon frequency ($\omega_{\log}$). To date, several high- T_c binary lithium-rich HPE superconductors have been discovered [19–21], but none have yet been reported with a T_c exceeding 100 K. Enhancing the T_c of binary lithium-rich HPE superconductors remains a key challenge in this field. To address this issue, it is crucial to enhance the coupling between NNAs and phonons, particularly by enabling more electrons and phonons across a broader frequency range to participate in EPC, on the basis of the reported relationship between superconductivity and NNAs and lattice vibrational modes in binary lithium-rich HPEs. The binary lithium-rich HPE superconductor Li_8Au , which consists of lithium and the transition metal gold (Au) [17], demonstrates better superconducting performance than other lithium-rich HPE superconductors with elements such as P [8,21], As [18], Se [14], Te [15], and Pb [22]. This occurs due to enhanced hybridization between NNAs and atoms near the E_F . Therefore, adjusting the hybridization between transition metal elements and NNAs could be a promising strategy for further increasing the T_c of binary lithium-rich HPEs.

In Li_8Au , strong hybridization occurs between the NNAs and the atomic orbitals. However, the van Hove singularity (VHS) is located approximately 1 eV below E_F . To bring the VHS closer to the Fermi level, we explored lithium-rich compounds with transition metal elements from lower groups. In lithium-rich Li–Pt (Group VIIb, 10) compounds, p orbitals become significant under pressures of approximately 10 GPa [23]. In contrast, no notable p orbital contributions near E_F were observed in the Li–Fe (Group VIIb, 8) system [24]. Notably, increasing pressure tends to localize the d orbitals of transition metals, thereby promoting p -state electrons to act as valence electrons [25,26]. To achieve concurrent hybridization of p -state and d -state electrons with NNAs, we selected rhodium (Rh), a Group VIIb, nine transition metals from the fifth period, to form lithium-rich Li–Rh compounds for further investigation.

In this work, to explore pathways for further increasing the T_c of binary lithium-rich HPEs, we focused on investigating high-pressure lithium-rich compounds involving the transition metal rhodium. We systematically explored the crystal structures and phase transitions of Li–Rh compounds under high pressure via crystal structure prediction methods and first-principles calculations. A novel HPE superconductor, Li_4Rh , was predicted. Two stable phases of Li_4Rh with $Cmcm$ and $I4/mmm$ space groups, consisting of alternating layers of Li and Rh atoms, are identified above 150 GPa. Li_4Rh undergoes a phase transition from $Cmcm$ to $I4/mmm$ at 256 GPa. These two phases exhibit NNAs near the Fermi level and display deformed cylindrical Fermi surfaces. The large and closed Fermi surface allows phonons with a wide range of q vectors (i.e., a broad frequency range) to participate in EPC, and hybridization between NNAs and atoms near the Fermi level induces strong EPC. Notably, $I4/mmm$ - Li_4Rh has a strong EPC and high $\omega_{\log}$, resulting in a high T_c of approximately 108.2 K at 300 GPa, surpassing the temperature of liquid nitrogen. To our knowledge, $I4/mmm$ - Li_4Rh is the first HPE superconductor predicted with a T_c exceeding 100 K. Our findings provide a valuable guide for future research into high- T_c electrides.

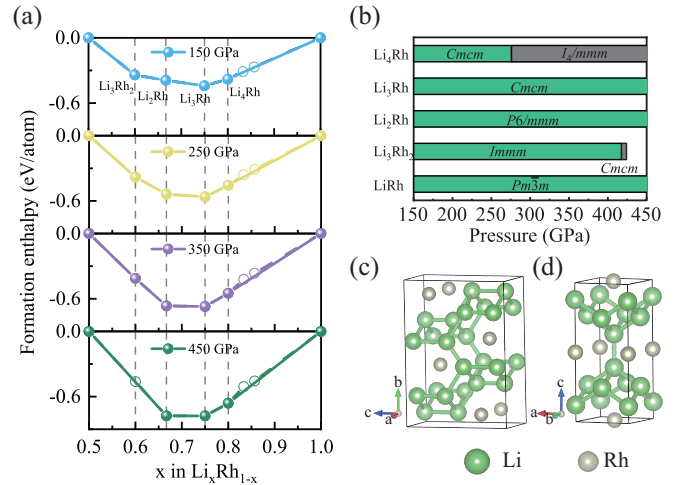


FIG. 1. Energetic stability of the Li–Rh compounds under pressure and the crystal structures of Li_4Rh . (a) Convex hull of Li–Rh compounds at various pressures. The solid Li and LiRh at selected pressures are used as references. The solid and open symbols represent thermodynamically stable and unstable compositions, respectively. (b) Pressure-composition phase diagram for Li–Rh compounds. Different colors are used to distinguish the different phases. The crystal structure of (c) $Cmcm$ Li_4Rh at 150 GPa and (d) $I4/mmm$ Li_4Rh at 300 GPa.

Herein, we explored lithium-rich Li–Rh compounds under high pressure via swarm intelligence-based CALYPSO [27,28] and the evolutionary algorithm USPEX [29], as lithium-rich compounds are more likely to form electrides. To evaluate the stability of the predicted lithium-rich compounds, the formation enthalpies related to decomposition into the most stable phases of Li and LiRh in the corresponding pressure range are calculated. The calculated results at various pressures are shown in the convex hull [Fig. 1(a)]. Several thermodynamically stable lithium-rich Li–Rh compounds with stoichiometries of Li_3Rh_2 , Li_2Rh , Li_3Rh , and Li_4Rh are predicted. The predicted pressure-composition phase diagram of these compounds is shown in Fig. 1(b). At the selected pressures, LiRh stabilizes into a cubic structure with a $Pm\bar{3}m$ space group (Fig. S1 [30]). Notably, $P6/mmm$ - Li_2Rh and $Cmcm$ - Li_3Rh maintain their stability in the pressure range of 150–450 GPa. $Immm$ - Li_3Rh_2 undergoes a phase transition at approximately 418 GPa, transforming into a new high-pressure phase, $Cmcm$ - Li_3Rh_2 , which remains stable below 425 GPa. $Cmcm$ - Li_4Rh is thermodynamically stable below 256 GPa, and $I4/mmm$ - Li_4Rh remains stable at higher pressures, extending to at least 450 GPa. All optimized structures are shown in Fig. 1 and Figs. S1 and S2 in the Supplemental Material [30]. The detailed lattice constants and atomic Wyckoff positions of these stable compounds are summarized in Table S1. No imaginary frequency appears in the phonon dispersion, indicating lattice dynamic stability (Fig. S3 [30]).

All the lithium-rich Li–Rh compounds feature stacked geometries, with alternating layers of Li and Rh atoms (Figs. S1, S2, and S4 [30]). As the Li content increases, structural reorganization occurs in 2D sheets composed of Li atoms. In $Immm$ - Li_3Rh_2 , the Li sheets are composed of four- and six-

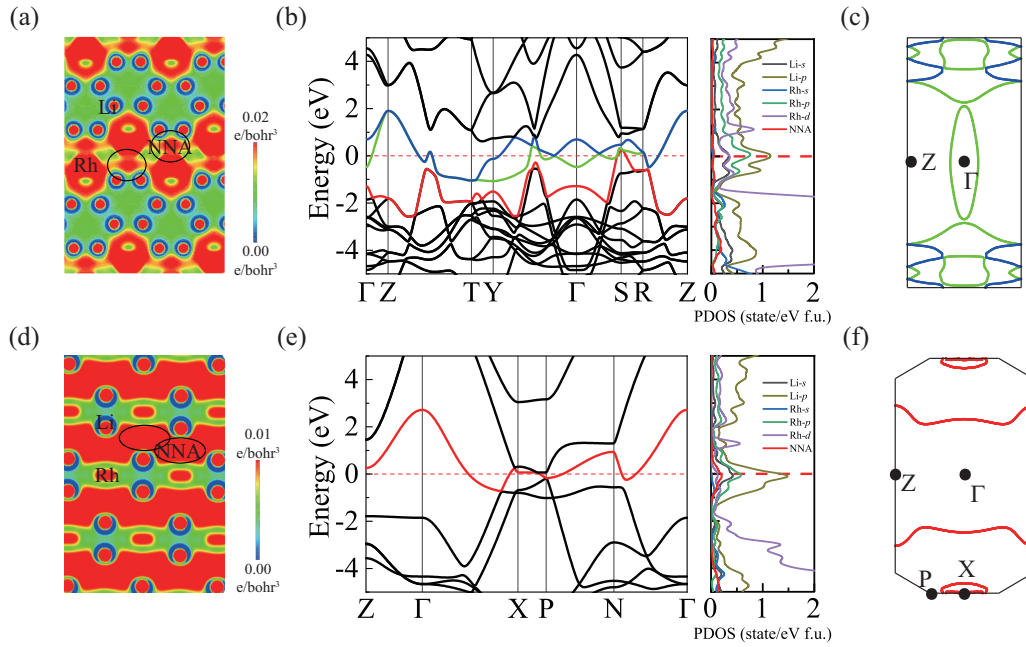


FIG. 2. Electronic structures of *Cmc*-Li₄Rh and *I4/mmm*-Li₄Rh. 2D partial charge density maps corresponding to the bands that cross the Fermi level for the (a) (100) plane of *Cmc*-Li₄Rh at 150 GPa and for the (d) (110) plane of *I4/mmm*-Li₄Rh at 300 GPa. The NNAs are marked with black ovals. (b) Electronic band structure and partial density of states and (c) 2D Fermi surfaces of the (1 $\bar{1}$ 0) plane for *Cmc*-Li₄Rh at 150 GPa. (e) Electronic band structure and partial density of states and (f) 2D Fermi surfaces of the (1 $\bar{1}$ 0) plane for *I4/mmm*-Li₄Rh at 300 GPa. Red, green, and blue represent different bands crossing the Fermi level, whereas black indicates the bands that do not cross the Fermi level.

membered rings, whereas *P6/mmm*-Li₂Rh has 2D sheets with hexagonal rings. Notably, the application of pressure results in atomic dislocations in the Li and Rh layers, leading to the formation of a six-membered ring in *Cmc*-Li₃Rh₂. In lithium-rich Li₃Rh and Li₄Rh, the Li sheets have a zigzag pattern that accommodates more Li atoms (Figs. S2 and S4 [30]). Moreover, the zigzag Li sheets combined with Rh atoms form many lattice interstitials in Li₃Rh and Li₄Rh. These interstitials promote the formation of NNAs. Notably, no NNAs are found in LiRh, Li₃Rh₂, Li₂Rh, or Li₃Rh. In *Cmc*-Li₃Rh, the scarcity of electrons hinders the formation of NNAs within the interstitials. Conversely, Li₄Rh, which possesses one additional electron relative to Li₃Rh, has NNAs in the interstitial space (Fig. S4 [30]). The NNAs in Li₄Rh are distributed near the Li sheets and exhibit various morphologies as a result of the interstitials. The NNAs manifested as pie-shaped structures in *I4/mmm*-Li₄Rh, whereas the NNAs presented bars of varying dimensions in *Cmc*-Li₄Rh. Among the lithium-rich Li-Rh compounds, the HPE Li₄Rh with unique NNAs provides us with an opportunity to study the superconductivity of HPEs.

To understand the electronic properties of the lithium-rich HPE Li₄Rh, we investigated the electronic structures near the Fermi level (E_F). The computed partial charge density near E_F reveals that hybridization occurs between NNAs and Rh, as well as between NNAs and Li, due to the entanglement of NNAs-Rh and NNAs-Li electrons [Figs. 2(a) and 2(d)]. Interestingly, the NNAs linked together to form 2D NNAs near E_F in *I4/mmm* Li₄Rh are different from the isolated NNAs in ELF. Notably, Li₄Rh may exhibit superconductivity owing to the hybridization between NNAs and Rh, as well as between NNAs and Li, which is also observed in Li₈Au [17].

Additionally, there are significant coupling peaks in the *s* and *p* orbitals of Li, the *p* and *d* orbitals of Rh, and the NNAs near the E_F in Li₄Rh. Notably, compared with those in *Cmc* Li₄Rh, the NNAs in *I4/mmm* Li₄Rh near the E_F exhibit stronger hybridization between NNAs and atoms because of the greater density of states (DOS) [Figs. 2(b) and 2(e)]. Three narrow bands in *Cmc*-Li₄Rh and one narrow band, *I4/mmm*-Li₄Rh, across E_F indicate that *Cmc*-Li₄Rh and *I4/mmm*-Li₄Rh are metallic. Notably, the Γ in the reciprocal space is surrounded by the closed and large Fermi surfaces in the *Cmc* and *I4/mmm* phases of Li₄Rh. The Fermi surfaces in these phases exhibit a cylindrical shape along the Γ -Z direction [Figs. 2(c) and 2(f)]. The area of the cylindrical Fermi sheet in *Cmc* Li₄Rh is 6.59 Å⁻², and that in the *I4/mmm* phase is 11.59 Å⁻². However, a partition appears in the middle of the Fermi surface in the *Cmc* phase, dividing this cylinder into three parts. Additionally, some Fermi sheets are observed at the edge of the first Brillouin zone in both phases. Moreover, Li₄Rh simultaneously features flat bands (*T*-*Y*, *S*-*R* paths in *Cmc*-Li₄Rh, *X*-*P* paths in *I4/mmm*-Li₄Rh) and steep bands (Γ -*Z*-*T*, *R*-*Z* paths in *Cmc*-Li₄Rh, Γ -*X*, *N*- Γ paths in *I4/mmm*-Li₄Rh). Overall, the hybridization between NNAs and atoms near the Fermi level encouraged us to further investigate the superconductivity of Li₄Rh.

To explore the superconductivity of HPE Li₄Rh, we performed EPC calculations [31,32]. The calculated EPC constant λ and the logarithmic average phonon frequency $\omega_{\log}$ are approximately 1.01 and 342.5 cm⁻¹ (492.8 K) for *Cmc*-Li₄Rh at 150 GPa and 2.21 and 424.5 cm⁻¹ (610.8 K) for *I4/mmm*-Li₄Rh at 300 GPa [Figs. 3(a) and 3(b)]. Notably, a high $\omega_{\log}$ for *I4/mmm*-Li₄Rh at 300 GPa is rare among all past HPE superconductors [8,17].

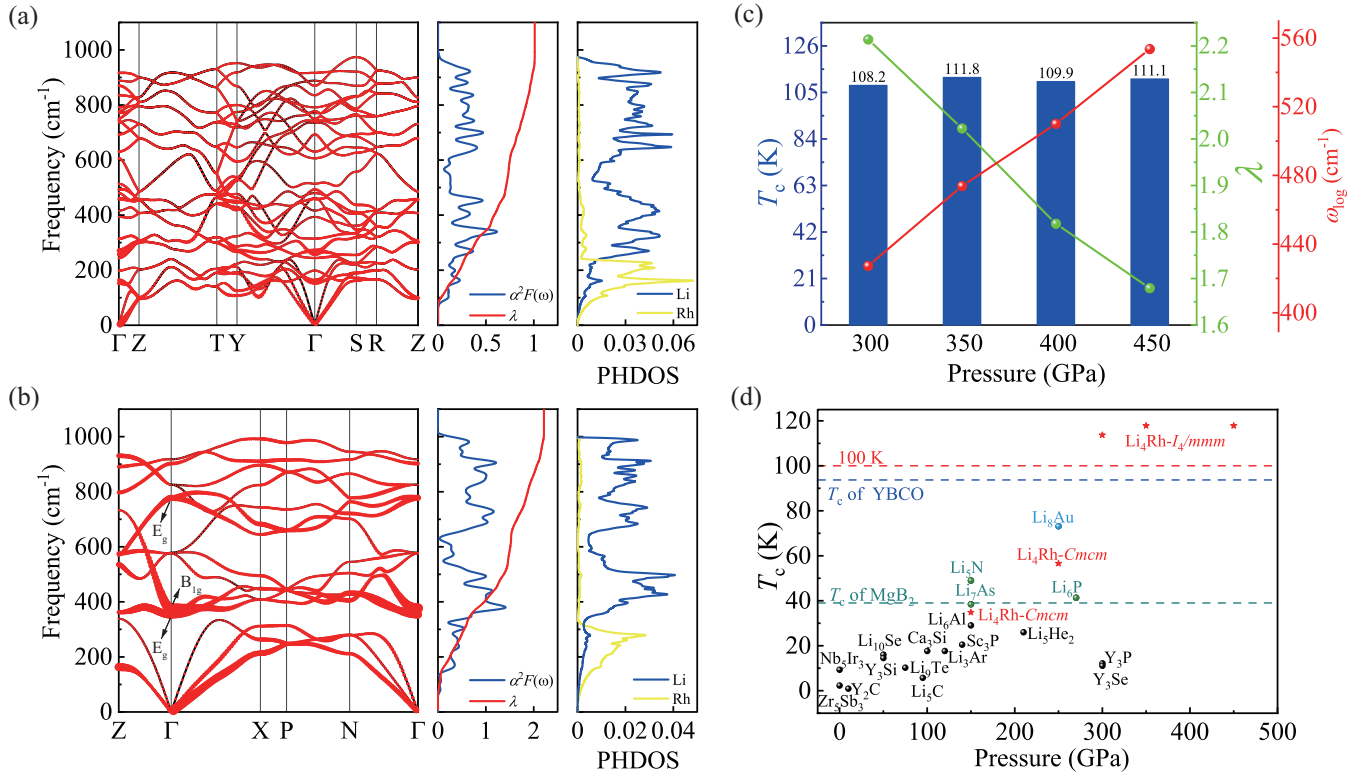


FIG. 3. Superconducting properties of *Cmcu* Li₄Rh and *I4/mmm* Li₄Rh. (a) Phonon dispersion relationships, projected phonon density of states (PHDOS), Eliashberg spectral function $\alpha^2 F(\omega)$, and EPC parameter $\lambda(\omega)$ for (a) *Cmcu* Li₄Rh at 150 GPa and (b) *I4/mmm* Li₄Rh at 300 GPa. The size of the solid dots on the phonon spectra signifies the contribution to EPC ($\lambda_{q,v}$). (c) Calculated λ , $\omega_{\log}$, and T_c of *I4/mmm* Li₄Rh at different pressures. (d) T_c -pressure diagram for representative superconducting electrides.

The T_c values of the HPE Li₄Rh are calculated via the McMillan-Allen-Dynes formula [31,32]. Using a Coulomb pseudopotential of $\mu^* = 0.1$, the highest T_c value estimated was 34.9 K for *Cmcu*-Li₄Rh at 150 GPa and 108.2 K for *I4/mmm*-Li₄Rh at 300 GPa. *I4/mmm*-Li₄Rh displays a T_c of 111.8 K at 350 GPa [Fig. 3(c)]. Considering the semiempirical nature of the Coulomb pseudopotential [33], the calculated T_c values with μ^* values in the range of 0.06–0.30 are estimated to be between 58.9 and 130.5 K at 350 GPa for *I4/mmm*-Li₄Rh (Fig. S6 [30]). Notably, the T_c exhibits an inverse correlation with the μ^* . Moreover, within the framework of superconducting density functional theory, we obtain a T_c of 113.2 K at 350 GPa by solving the gap equation using the superconducting-Toolkit package [34,35]. The T_c values obtained using both methods are consistent, supporting the validity of our calculations. Notably, the T_c for *I4/mmm*-Li₄Rh surpasses the highest T_c reported for electrides [Fig. 3(d)] [36–45] and is higher than the T_c of Rh-H compounds [~ 6 K for $P2_1/m$ -RhH₂] [46].

Notably, similar electronic structures exist in *Cmcu*-Li₄Rh and *I4/mmm*-Li₄Rh, but the T_c and λ for *I4/mmm*-Li₄Rh are much greater than those of *Cmcu*-Li₄Rh. This phenomenon can be attributed to stronger hybridization between the NNAs and atoms near E_F and a larger closed Fermi surface in *I4/mmm*-Li₄Rh. First, compared with those in *Cmcu*-Li₄Rh, NNAs in *I4/mmm*-Li₄Rh have stronger hybridization near the Fermi level, indicating that NNAs near E_F have stronger interactions with atoms. This stronger interaction promotes

the pairing of electrons and phonons. Second, the number of cylindrical Fermi sheets in *I4/mmm*-Li₄Rh is greater than that in *Cmcu*-Li₄Rh. These closed Fermi sheets create favorable conditions for the occurrence of the Kohn anomaly. The Kohn anomaly [47,48] typically occurs only when there are two electronic states, k_1 and $k_2 = k_1 + q$, both on the Fermi surface, that affect the vibrations at specific wave vectors q points in the Brillouin zone. The closed Fermi sheet allows q vectors pointing to the center of areas circled by the Fermi sheet to find the corresponding k_1 and k_2 values on this Fermi sheet. The larger the area of the closed Fermi sheet is, the more electronic states interact with phonons, contributing to EPC. Notably, significant accumulation of EPC occurs near the center of the cylindrical Fermi surfaces in *Cmcu*-Li₄Rh at 150 GPa and in *I4/mmm*-Li₄Rh at 350 GPa, particularly around the Γ point (Fig. S7 [30]). Thus, owing to the larger closed Fermi sheet, λ is greater in *I4/mmm*-Li₄Rh than in *Cmcu*-Li₄Rh. Overall, the EPC of *I4/mmm*-Li₄Rh is greater than that of *Cmcu*-Li₄Rh because of the stronger hybridization of NNA with atoms near E_F and the larger enclosed Fermi sheet. Considering the outstanding superconductivity of *I4/mmm*-Li₄Rh, we further explore the superconductivity below.

The phonon dispersions of *I4/mmm*-Li₄Rh exhibit significant irregularities, with the optical branches softening around the Γ point, particularly for the E_g and B_{1g} modes, which notably contribute to the EPC [Fig. 3(b)]. This phonon softening is clearly attributed to the Kohn anomaly. The two

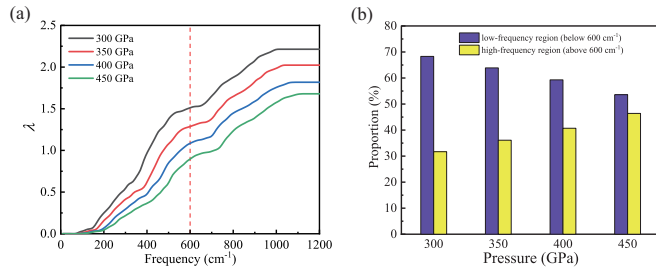


FIG. 4. EPC properties of $I4/mmm$ -Li₄Rh under high pressure. (a) EPC parameter $\lambda(\omega)$ for $I4/mmm$ -Li₄Rh at various pressures. (b) Contributions of different frequency regions to the total λ in $I4/mmm$ -Li₄Rh at various pressures.

phonon modes responsible for softening primarily involve the vibrations of Li atoms (Fig. S8). However, the EPC is not entirely confined to this frequency range but is instead distributed fairly uniformly across the phonon frequency spectrum [Figs. 3(a) and 3(b)]. The involvement of many high-frequency phonons in the EPC justifies the high value of $\omega_{\log}$. Notably, the EPC strength, λ , plateaus at approximately 600 cm⁻¹ and above 1000 cm⁻¹, corresponding to regions lacking phonon density of states (PHDOS).

To further investigate the role of Fermi surface nesting in the EPC, we computed the Fermi surface nesting function at different pressures (Fig. S9). However, the peak shift of the strong Fermi surface nesting did not lead to a corresponding shift in the EPC (Fig. S10). Therefore, the EPC in $I4/mmm$ -Li₄Rh is driven primarily by the Kohn anomaly, which occurs across a broad frequency range of phonon modes. Despite the widespread presence of Kohn anomalies within the cylindrical Fermi sheet, the specific q -vector locations of these anomalies cannot be clearly identified. Similar phenomena were observed in MgB₃ [49]. Furthermore, the normalized quasiparticle density of states ($\frac{N_s(\omega)}{N_F} = \text{Re}[\frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}}]$) shows a single pair of peaks (Fig. S11), indicating that $I4/mmm$ -Li₄Rh behaves as a single-gap (21.4 meV) superconductor. Notably, the gap $\Delta(k)$ significantly varies across the cylindrical shape of the Fermi surface sheet [Figs. S12(a) and S12(c) [30]], whereas the Fermi velocities remain relatively constant across the sheet (Fig. S5). A similar phenomenon, where the relationship between the Fermi surface and superconducting gap is less robust, is also observed in well-known MgB₂ [50]. Notably, the EPC distribution on the Fermi surface was calculated, revealing a strong correlation between λ_k and $\Delta(k)$ (Fig. S12).

Unlike other well-known HPE superconductors (Li₆P, Li₈H₄, Li₈Au, and Li₁₀As), in which the T_c rapidly increases with increasing EPC [8,13,16–18], the T_c of $I4/mmm$ -Li₄Rh remains stable because the logarithmic average phonon frequency increases as the EPC strength decreases. Although the trend in λ with frequency remains nearly unchanged, the pressure-induced upshift in the lattice vibrational frequency [16,51] results in a partial absence of EPC in the low-frequency region (below 600 cm⁻¹) [Fig. 4(a)]. Notably, the low phonon density of states at different pressures results in a weak EPC near the 600 cm⁻¹ and 1100 cm⁻¹ frequencies (Fig. S10). However, the high-pressure $I4/mmm$ -Li₄Rh

features a significantly larger closed Fermi surface, indicating a large magnitude for $k_2 - k_1$, which allows a wider range of q -vectors to participate in intraband EPC. Consequently, a broader range of phonon frequencies contributes to EPC in $I4/mmm$ -Li₄Rh at high pressure [Fig. 3(b)], allowing high-frequency phonons (above 600 cm⁻¹) to engage in EPC. Thus, the contribution of λ in the high-frequency region to the total λ [Fig. 4(b)] increases, ultimately suggesting an increase in $\omega_{\log}$. Specifically, as pressure increases, λ in the high-frequency region remains nearly constant, whereas λ in the low-frequency region decreases (Fig. S13), leading to an increased proportion of λ in the high-frequency region. Compared with other HPE superconductors, the logarithmic average phonon frequency becomes a key factor in determining the superconductivity of $I4/mmm$ -Li₄Rh. Overall, the large and closed Fermi sheet in $I4/mmm$ -Li₄Rh results in strong EPC and high $\omega_{\log}$, resulting in the highest T_c among electrides. Therefore, we propose that HPEs with large and closed Fermi surfaces, which induce strong EPC and allow a wider range of q vectors to participate in intraband EPC, are more likely to exhibit high T_c .

The superconductivity of nonelectride compounds in the Li-Rh system (LiRh, Li₃Rh₂, Li₂Rh, Li₃Rh) was examined. However, further calculations reveal that superconductivity is observed only in Li₃Rh. The bands crossing the Fermi level are attributed primarily to electrons from the Li- s and p orbitals, as well as the Rh- p and d orbitals (Fig. S14). The calculated T_c at 350 GPa is 6.3 K (with $\mu^* = 0.1$). Li₃Rh has a high $\omega_{\log}$ of 528.2 cm⁻¹ (759.9 K), but its lower λ value of 0.46 results in a much lower T_c than that of Li₄Rh (Fig. S15 [30]). The reduced λ in Li₃Rh is attributed to the absence of NNAs, which limits the electron source available for EPC. Therefore, NNAs play a crucial role in driving the EPC in the electride compounds of the Li-Rh system.

In summary, we systematically explored the crystal structures and phase transitions of Li-Rh compounds under high pressure via crystal structure prediction methods and first-principles calculations. We predicted an HPE superconductor, $I4/mmm$ -Li₄Rh, characterized by 2D NNAs near E_F . Notably, $I4/mmm$ -Li₄Rh has a strong EPC and a high logarithmic average phonon frequency, which results in a high T_c of approximately 108.2 K at 300 GPa, surpassing the temperature of liquid nitrogen. To our knowledge, $I4/mmm$ -Li₄Rh is the first HPE superconductor predicted with a T_c exceeding 100 K. Unlike other well-known HPE superconductors, in which the T_c rapidly increases with increasing EPC, the T_c of $I4/mmm$ -Li₄Rh remains stable because the logarithmic average phonon frequency increases as the EPC strength decreases. Consequently, the logarithmic average phonon frequency becomes a key factor in determining the superconductivity of $I4/mmm$ -Li₄Rh. Our analysis reveals that strong hybridization between NNAs and atoms near the Fermi level is the key for EPC and that the deformed cylindrical Fermi surface allows a wide range of q vectors to participate in EPC, which in turn involves a broader spectrum of phonon frequencies. We propose that HPEs with a large and closed Fermi sheet and strong hybridization between NNAs and atoms near the Fermi level are more likely to exhibit high T_c . Our findings provide valuable guidance for future research into high- T_c electrides.

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- Fermi nesting function; phonon dispersion relationships, projected phonon density of states (PHDOS), Eliashberg spectral function $\alpha^2F(\omega)$, and EPC parameter; normalized quasiparticle density of states; λ of different frequency regions; electronic band structure and partial density of states, which also contains Refs. [52–58].
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