Microscopic mechanism of room-temperature superconductivity in compressed LaH$_{10}$

Liangliang Liu,1,2 Chongze Wang,1 Seho Yi,1 Kun Woo Kim,3 Jaeyong Kim,1 and Jun-Hyung Cho1,*

1Department of Physics, Research Institute for Natural Science, and HYU-HPSTAR-CIS High Pressure Research Center, Hanyang University, 222 Wangsimni-ro, Seongdong-Ka, Seoul 04763, Republic of Korea
2Key Laboratory for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, People’s Republic of China
3Center for Theoretical Physics of Complex Systems, Institute for Basic Science, Daejeon 34051, Republic of Korea

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Room-temperature superconductivity has been one of the most challenging subjects in modern physics. Recent experiments reported that lanthanum hydride LaH$_{10x}$ (x < 1) raises a superconducting transition temperature $T_c$ up to $\sim$260 (or 250) K at high pressures around 190 (170) GPa. Here, based on first-principles calculations, we reveal that compressed LaH$_{10}$ has symmetry-protected Dirac-nodal-line states, which split into hololeike and electronlike bands at the high-symmetry points near the Fermi energy ($E_F$), thereby producing a van Hove singularity (vHs). The crystalline symmetry and the band topology around the high-symmetry points near $E_F$ are thus demonstrated to be important for room-temperature superconductivity. Further, we identify that the electronic states at the vHs are composed of strongly hybridized La $f$ and H $s$ orbitals, giving rise to a peculiar characteristic of electrical charges with anionic La and both anionic and cationic H species. Consequently, a large number of electronic states at the vHs are strongly coupled to the H-derived high-frequency phonon modes that are induced via the unusual, intricate bonding network of LaH$_{10}$, therefore yielding a high $T_c$. Our findings elucidate the microscopic mechanism of the observed high-$T_c$ BCS-type superconductivity in LaH$_{10}$, which can be generic to another recently observed high-$T_c$ hydride H$_3$S.

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Ever since the first discovery of superconductivity (SC) in 1911 [1], scientists have searched for materials that can conduct electricity without resistance below a superconducting transition temperature $T_c$. So far, tremendous efforts have been devoted to exploring high-$T_c$ SC in a variety of materials such as cuprates [2], pnictides [3], and hydrogen-rich compounds (called hydrides) [4–7]. Among them, SC in hydrides has been successfully explained by the Bardeen-Cooper-Schrieffer (BCS) theory [8], where SC is driven by a condensate of electron pairs, so-called Cooper pairs, due to electron-phonon interactions. The pioneering idea that hydrogen can be a good candidate for high-$T_c$ SC was proposed by Ashcroft [9], i.e., metallic hydrogen with light atomic mass is expected to have high vibrational frequencies, thereby providing a high $T_c$ due to a strong electron-phonon coupling (EPC). However, the metallization of hydrogen is very difficult to achieve experimentally, because it requires too high pressures over $\sim$400 GPa [10–12]. Instead, high-$T_c$ SC in hydrides can be realized at relatively lower pressures that are currently accessible using static compression techniques [13]. Motivated by theoretical predictions of high-$T_c$ SC in many hydrides [6,14–16], experiments were performed to confirm that compressed sulfur hydride H$_2$S exhibits a $T_c$ of 203 K at pressures around 150 GPa [17]. Recently, x-ray diffraction and optical studies demonstrated that lanthanum (La) hydrides can be synthesized in an fcc lattice at $\sim$170 GPa upon heating to $\sim$1000 K [18], consistent with the earlier predicted cubic metallic phase of LaH$_{10}$ having cages of 32 H atoms surrounding an La atom [see Fig. 1(a)] [6,7]. Subsequently, two experimental groups nearly simultaneously reported that such an La hydride LaH$_{10x}$ (x < 1) exhibits a high $T_c$ of $\sim$260 K at pressures of $\sim$190 GPa or 250 K at $\sim$170 GPa [19–23]. Although this observed room-temperature SC in LaH$_{10x}$ has been explained in terms of conventional superconductivity described by the BCS theory [6,7], a microscopic understanding of why LaH$_{10}$ features a strong EPC is still missing.

To explore the microscopic mechanism of the high-temperature BCS-type SC in compressed LaH$_{10}$, we here, based on first-principles calculations, not only investigate the salient characteristics of electronic, bonding, and phononic properties, but also identify which electronic states are coupled with H-derived high-frequency phonon modes. We reveal that LaH$_{10}$ has symmetry-protected topological Dirac-nodal-line (DNL) states including seven one-dimensional (1D) dispersive nodal lines around $E_F$. Remarkably, four DNLs split into hololeike and electronlike bands at the four equivalent high-symmetry points on the Brillouin zone boundary near $E_F$, creating a vHs. The resulting significant increase in the electronic density of states at $E_F$, which is the key ingredient for room-temperature SC, can thus originate from the crystalline symmetry and the band topology around the high-symmetry points. We further find that the electronic states near $E_F$ exhibit a strong hybridization of the La 4$f$ and H $s$ orbitals, giving rise to a peculiar electrical charge characteristic of anionic La and both anionic H$_1$ and cationic H$_2$ atoms. This unusual, intricate bonding network of LaH$_{10}$ with the La-H$_1$ covalent bonds induces the high-frequency vibrations of H atoms, which are, in turn, strongly coupled to large numbers of hybridized La 4$f$ and H $s$ electronic states at the vHs. The resulting strong EPC significantly enhances $T_c$, as measured by recent experiments [19–21]. Therefore, our findings shed...
The dashed line represents the (1\bar{1}0) face. The H atoms located on the (1\bar{1}0) face are indicated by the arrows. (b) Total charge density \( \rho_{\text{tot}} \) of LaH\textsubscript{10}, plotted on the (1\bar{1}0) face. In (b), the contour spacing is 0.13 e/Å\textsuperscript{3}. The center of the void space surrounded by eight neighboring H\textsubscript{1} atoms is marked “\texttimes” in (b).

Our density-functional theory (DFT) calculations were performed using the Vienna \textit{ab initio} simulation package with the projector augmented-wave method [24–26]. For the exchange-correlation energy, we employed the generalized-gradient approximation functional of Perdew-Burke-Ernzerhof (PBE) [27]. A plane-wave basis was taken with a kinetic energy cutoff of 500 eV. The \textit{k-space} integration was done with 16 × 16 × 16 k points (in the Brillouin zone) for the structure optimization and 70 × 70 × 70 k points for the density of states (DOS) calculation. All atoms were allowed to relax along the calculated forces until all the residual force components were less than 0.005 eV/Å. We construct Wannier representations by projecting the Bloch states from the first-principles calculations of bulk materials onto H s and La s, p, d, and f orbitals, and generate a tight-binding Hamiltonian with a basis of maximally localized Wannier functions [28]. Using the QUANTUM ESPRESSO package [29], we take the 6 × 6 × 6 \( g \) points and 24 × 24 × 24 \( k \) points for the computation of the phonon frequencies, while the 24 × 24 × 24 \( g \) points and 72 × 72 × 72 \( k \) points for the EPC constants.

We begin by optimizing the structure of compressed LaH\textsubscript{10} at 300 GPa using the DFT calculation. Figure 1(a) shows the optimized fcc LaH\textsubscript{10} structure, which has the lattice parameters \( a = b = c = 4.748 \) Å. We find that the H\textsubscript{1}-H\textsubscript{1} bond length \( d_{11} \) is 1.145 Å, slightly longer than the H\textsubscript{1}-H\textsubscript{2} bond length \( d_{22} = 1.064 \) Å. These values are in good agreement with those \( d_{11} = 1.152 \) Å and \( d_{22} = 1.071 \) Å of a previous DFT calculation [6] performed at 300 GPa. The calculated total charge density \( \rho_{\text{tot}} \) of LaH\textsubscript{10} is displayed in Fig. 1(b). It is seen that H atoms in the H\textsubscript{2} cage are bonded to each other with covalent bonds. Here, each H-H bond has a saddle point of charge density at its midpoint, similar to the C-C covalent bond in diamond [30]. The charge densities at the midpoints of the H\textsubscript{1}-H\textsubscript{1} and H\textsubscript{1}-H\textsubscript{2} bonds are 0.74 and 0.91 e/Å\textsuperscript{3}, respectively. The relatively weaker H\textsubscript{1}-H\textsubscript{1} covalent bond is well represented by its larger value of \( d_{11} \) than \( d_{22} \). Interestingly, the electrical charges of La and H\textsubscript{1} atoms are connected with each other, indicating a covalent character of the La-H\textsubscript{1} bonds. We note that for other La hydrides such as LaH\textsubscript{2}sex, with fluorite-type structures [31], a charge transfer occurs from La to H atoms, thereby resulting in cationic La and anionic H. But surprisingly, compressed LaH\textsubscript{10} is found to exhibit a drastically different feature of electrical charges, i.e., anionic La and both anionic H\textsubscript{1} and cationic H\textsubscript{2}, as discussed below. This unusual, intricate bonding network of LaH\textsubscript{10} contrasts with the previously proposed bonding nature based on a simple charge transfer picture from cationic La to anionic H [7].

Figures 2(a) and 2(b) show the calculated band structure and partial DOS of LaH\textsubscript{10}, respectively. The band projections onto the H s and La f orbitals are displayed in Fig. 2(a). Compared to other orbitals, these two orbitals are more dominant components of the electronic states located near \( E_{\text{F}} \) (see Fig. S1 of the Supplemental Material [32]). In Fig. 2(a), the band dispersion around the \( L \) point (just below \( E_{\text{F}} \)) shows the presence of holelike and electronlike bands along the \( \overline{LH} \) symmetry line, giving rise to an equal vHs around the four symmetry-equivalent \( L \) points [see Fig. 2(c)] in the first Brillouin zone. Using the local principal-axis coordinates, we obtain the effective masses \( m_{1} \), \( m_{2} \), and \( m_{3} \) of the hololike band as \(-0.10m_{e}, -1.05m_{e}, -6.95m_{e}\) (thermal mass \( m_{\text{th}} \equiv |m_{1}m_{2}m_{3}|^{1/3} \equiv 1.06m_{e}\)), while we obtain those of electronlike band as \(-0.09m_{e}, 0.79m_{e}, 0.20m_{e}\) (\( m_{\text{th}} = 0.24m_{e}\)). Note that the larger the thermal mass, the flatter is the hole- or electronlike band. The inset of Fig. 2(b) displays a closeup of the total DOS around the vHs, which represents the presence of two van Hove singularities separated by \( \Delta E_{\text{vH}} \equiv 90 \) meV. Recently, Quan and Pickett [33] pointed out the importance of such a double-shaped vHs in increasing \( T_{c} \) of compressed H\textsubscript{3}S, where the values of \( m_{\text{th}} \) are 0.42\( m_{e} \) and 0.31\( m_{e} \) at the two vHs points (with \( \Delta E_{\text{vH}} \equiv 300 \) meV), respectively. We note that the formation of the vHs is associated with the band splitting from the...
symmetry-protected DNLs at the high-symmetry points, as discussed below. Thus, the two recently observed high-\(T_{c}\) hydrides, \(\text{H}_3\text{S} [17]\) and \(\text{LaH}_{10} [19,20]\), have similar electronic features such as DNLs and double-shaped vHs (see Fig. S2 of the Supplemental Material), which can be rather generic to high-\(T_{c}\) superconductivity. It is noteworthy that high-symmetry metallic hydrides having such vHs with large \(m_{0}\) can increase their electronic density of states in proportion to the number of equivalent high-symmetry points around which the vHs is created, leading to a strong EPC. Interestingly, the PDOS projected onto the \(\text{H}_1\) s and \(\text{La} f\) orbitals exhibits sharp peaks close to \(E_{F}\) [see Fig. 2(b)], indicating a strong hybridization of the two orbitals. Compared to the \(\text{H}_1\) s orbital, the PDOS projected onto the \(\text{H}_2\) s orbital is much suppressed around \(E_{F}\). Such different aspects of the \(\text{H}_1\) and \(\text{H}_2\) s orbitals reflect their opposite charge characters, i.e., anionic \(\text{H}_1\) and cationic \(\text{H}_2\), which will be manifested below by a charge-density analysis. The same anionic character of \(\text{La}\) and \(\text{H}_1\) atoms is well consistent with the strong hybridization of \(\text{La}\) \(f\) and \(\text{H}_1\) s orbitals just below \(E_{F}\) [see Figs. 2(a) and 2(b)] that produces the formation of the La-\(\text{H}_1\) covalent bonds [see Fig. 1(b)].

It is remarkable that the hololeike and electronlike bands are degenerate at the \(L\) point to form a DNL along the \(\Gamma L\) line, showing the 1D nodal line with a large bandwidth \(\sim 6\ \text{eV}\) [see Fig. 2(a)]. Here, we emphasize that the hololeike and electronlike bands are split from the DNL bands, producing double-shaped vHs close to \(E_{F}\). Figure 2(c) displays all the DNLs near \(E_{F}\), which are computed by using the WANNIERTOOLS package [34]. Here, the tight-binding Hamiltonian with maximally localized Wannier functions [28] reproduces well the electronic bands obtained using the DFT calculation (see Fig. S3 of the Supplemental Material). Since the crystalline symmetry of \(\text{LaH}_{10}\) belongs to the space group \(\text{Fm} \overline{5} \text{m}\) (No. 225) with the point group \(O_h\), there are four and three DNLs along the symmetry-equivalent \(\Gamma L\) and \(\Gamma X\) lines [see Fig. 2(c)], respectively. It is noted that along the \(\Gamma L\) line, the system has threefold rotation symmetry (\(C_3\)) and an inversion (\(I\)). These spatial symmetries and time (\(T\)) reversal symmetry [35,36] allow two-dimensional irreducible symmetry representations to protect the DNL along the \(\Gamma L\) line. Similarly, the DNL along the \(\Gamma X\) line is protected by \(C_4\) and \(P T\). As shown in Fig. 2(d), we find that the band touching points along the DNLs exhibit large Berry curvature distributions. To find the topological characterization of the DNLs, we calculate the topological \(Z_2\) index [37], defined as \(\xi_1 = \frac{1}{2} \int_{\Gamma L} \text{det} \cdot \chi(k)\), along a closed loop encircling any of the DNLs. Here, \(\chi(k) = -i\langle \epsilon_{\text{H}_1} | \partial_{\text{H}_1} | \epsilon_{\text{H}_1} \rangle\) is the Berry connection of the related Bloch bands. We obtain \(\xi_1 = 1\) for the DNLs along the \(\Gamma L\) and \(\Gamma X\) lines, indicating that they are stable against perturbations without breaking rotational and \(P T\) symmetries. Nevertheless, we find that, when the spin-orbit coupling (SOC) is considered, the DNLs are fully gapped with small gaps [38] (see Fig. S4 of the Supplemental Material). Although the largest gap (\(\sim 125\ \text{meV}\)) is located at the \(L\) point, the total DOS around the vHs is similar to that obtained from the DFT calculation without including SOC (see Fig. S5 of the Supplemental Material), which may therefore hardly affect \(T_c\) of \(\text{LaH}_{10}\).

In order to examine the bonding character between the \(\text{La}\) atoms and the \(\text{H}_{32}\) cages, we calculate the charge-density difference, defined as \(\Delta \rho = \rho_{\text{oa}} - \rho_{\text{an}} - \rho_{\text{hit}},\) where the second and third terms represent the charge densities of the \(\text{LaH}_2\) lattice (i.e., \(\text{LaH}_2\) structure without \(\text{H}\) atoms) and the \(\text{LaH}_{10}\) lattice (\(\text{LaH}_2\) structure without \(\text{La}\) atoms), respectively. Figures 3(a)–3(c) show \(\rho_{\text{oa}},\rho_{\text{an}}\), and \(\Delta \rho\), respectively. Obviously, \(\Delta \rho\) illustrates that electron charge is transferred from the \(\text{H}_2\) atoms as well as the void space [marked “\(\times\)" region in Fig. 1(b), surrounded by eight neighboring \(\text{H}_1\) atoms] to the \(\text{La}\) and \(\text{H}_1\) atoms. Here, charge accumulation is also seen in the regions between \(\text{La}\) and \(\text{H}_2\) atoms, leading to their covalent bonding character. It is thus likely that the \(\text{La}\) and \(\text{H}_1\) atoms are characterized as being anionic, while the \(\text{H}_2\) atoms as being cationic. Such charge characters of \(\text{LaH}_{10}\) contrast with other \(\text{La}\) hydrides [31] that comprise cationic \(\text{La}\) and anionic \(\text{H}\) atoms. This drastic difference between \(\text{LaH}_{10}\) and other \(\text{La}\) hydrides can be ascribed to their different locations of \(\text{H}\) s orbitals. For \(\text{LaH}_{2+x}\) with fluoride-type structures [31], the \(\text{H}\) s orbital is located deeper than the \(\text{La} d\) or \(f\) orbitals, therefore inducing a charge transfer from \(\text{La}\) to \(\text{H}\) atoms. Meanwhile, as shown in Figs. 2(b) and 3(e), the PDOS of \(\text{LaH}_{10}\) and the \(\text{La}_2\text{H}_{10}\) lattice indicates that near \(E_F\), the \(s\) orbital of anionic \(\text{H}_1\) is more dominant than that of cationic \(\text{H}_2\). Consequently, in \(\text{LaH}_{10}\), the former \(s\) orbital hybridizes quite strongly with the \(\text{La} f\) orbitals to produce their PDOS peaks near \(E_F\) [see Fig. 2(b)] and the charge characteristics of anionic \(\text{La}/\text{H}_1\) and cationic \(\text{H}_2\) with the \(\text{La}-\text{H}_1\) covalent bonds are found to induce higher phonon frequencies of \(\text{H}_1\) atoms compared to \(\text{H}_2\) atoms, as demonstrated below. We also find that the frequencies of the \(\Gamma\)-phonon modes in the \(\text{La}_2\text{H}_{10}\) lattice without \(\text{La}\) atoms are much reduced, compared to those in \(\text{LaH}_{10}\) (see Fig. S6 of the Supplemental Material).

It has been known that the existence of vHs near \(E_F\) plays an important role in the BCS-type superconductivity [39–41]. To investigate how the electronic states around the vHs points are strongly coupled to phonon modes, we calculate the phononic properties of \(\text{LaH}_{10}\). Figure 4(a) shows the calculated phonon spectrum with the EPC strength, the phonon DOS projected onto selected atoms, and the Eliashberg function \(\alpha^2 F(\omega)\) with the integrated EPC constant \(\lambda(\omega)\). Our
results for the phonon dispersion and EPC strength are in good agreement with those obtained by a previous DFT calculation [6]. Interestingly, the phonon DOS is found to be divided into three regions I, II, and III [see Fig. 4(a)]. Here, region I is mostly contributed by the vibrations of La atoms, region II is due to a nearly equal mixture of vibrations from H1 and H2 atoms, and region III arises mainly from the vibrations of H2 atoms. Therefore, we estimate that the optical phonon modes of H1 atoms contribute to \( \sim 62\% \) of \( \lambda(\omega) \), while the acoustic (optical) phonon modes of La (H2) atoms contribute to \( \sim 18\% \) (20\%) of \( \lambda(\omega) \). This estimation indicates that H1-derived high-frequency optical phonon modes comprise a strong EPC with the electronic states at the vHs points, substantially contributing to the electronic, bonding, and phononic properties of the compressed fcc-LaH10. These two features cooperate to produce a strong EPC, thereby enhancing \( T_c \) in fcc-LaH10. We thus demonstrated that the crystalline symmetry, the band topology around the high-symmetry points near \( \Gamma \), and the peculiar bonding characters play crucial roles in achieving room-temperature SC in LaH10. Remarkably, two recently observed high-\( T_c \) hydrides, LaH10 and H3S, have similar electronic, bonding, and phononic characters such as the double-shaped vHs near \( \Gamma \), the La-H1 and S-H covalent bonds, and the H-derived high phonon frequencies. For LaH10 (H3S), the electronic states at the vHs points are likely coupled to the Fermi-surface nesting. In Fig. 4(b), we plot the Fermi surface with the major nesting vectors \( q_L \), \( q_X \), \( q_t \), and \( q_K \). Here, \( q_L \) and \( q_X \) match with the spanning vectors between the vHs points around the L points. For \( q_t \) and \( q_K \), the electronic states at the vHs points are likely coupled to the \( \Gamma \)-centered, polyhedron-shaped Fermi surface and the flat Fermi-surface portions, respectively, participating in EPC [see Fig. 4(b)]. Therefore, we can say that the coupling vectors between the vHs points and the Fermi surface account for the strong EPCs in the \( \Gamma \), \( X \), \( L \), and \( K \) points.

To conclude, our first-principles calculations for the electronic, bonding, and phononic properties of the compressed fcc-LaH10 phase have revealed two features that are of vital importance in increasing \( T_c \) of the BCS-type SC. One is the existence of vHs near \( \Gamma \), which originates from the hole-like and electron-like bands arising from the splitting of the symmetry-protected topological DNL states at the equivalent high-symmetry \( L \) points, and the other represents H-derived high vibrational frequencies that are induced via the unusual, intimate bonding network with anionic La and both anionic H1 and cationic H2 atoms. These two features cooperate to produce a strong EPC, thereby enhancing \( T_c \) in fcc-LaH10. We demonstrated that the crystalline symmetry, the band topology around the high-symmetry points near \( \Gamma \), and the peculiar bonding characters play crucial roles in achieving room-temperature SC in LaH10. Remarkably, two recently observed high-\( T_c \) hydrides, LaH10 and H3S, have similar electronic, bonding, and phononic characters such as the double-shaped vHs near \( \Gamma \), the La-H1 and S-H covalent bonds, and the H-derived high phonon frequencies. For LaH10 (H3S), the electronic states at the vHs points, which are mostly composed of hybridized La \( f \) and H1 \( s \) (\( p \) and \( H \) orbitals, effectively soften H-derived high-frequency phonon modes such as the stretching vibrations of the La-H1 (S-H) covalent bonds, leading to a strong EPC. It is noted that the fcc-LaH10 phase can be stabilized at higher pressures above \( \sim 170 \) GPa [18], while it is transformed into a lower-symmetry \( C2/m\)-LaH10 phase on decompression below 170 GPa [46]. Because of the disappearance of vHs near \( \Gamma \) in the \( C2/m\)-LaH10 phase [46], its \( T_c \) is expected to be lower than that of the fcc-LaH10 phase. As a matter of fact, recent experiments reported that \( T_c \) was observed to be \( \sim 215 \) K at \( \sim 150 \) GPa [21], which is lower than \( \sim 260 \) (250) K at \( \sim 190 \) (170) GPa [19,20]. The present findings not only provided a microscopic understanding of why compressed fcc-LaH10 features room-temperature SC with a strong EPC, but also will stimulate further research to...
explore other room-temperature superconductors from compressed hydrides.

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[32] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.99.140501 for the band projections onto all the H and La orbitals, the electronic bands obtained using the tight-binding Hamiltonian with maximally localized Wannier functions, the frequencies of the Γ-phonon modes in the LaHx, the band structure and DOS obtained with the inclusion of SOC, together with the results of band structure, PDOS, DNLs, and Berry curvature in H3S.