# **Supplemental Material**

### Emergent superconductivity in K<sub>2</sub>ReH<sub>9</sub> under pressure

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#### **Computational Details**

The structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations with the CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) method as implemented in the CALYPSO code.<sup>1, 2</sup> We carry out a structural search on K<sub>2</sub>ReH<sub>9</sub> at 0 K and selected pressures of 50, 100, 150, and 200 GPa. In the first step, random structures with certain symmetry are constructed, in which atomic coordinates are generated by crystallographic symmetry operations. Local optimizations using the VASP code<sup>3</sup> are done with conjugate gradients method and stopped when enthalpy changes became smaller than 1 ×  $10^{-5}$  eV per cell. After processing first generation structures, 60% of them with lower enthalpies are selected to construct the next generation with PSO (Particle Swarm Optimization).<sup>2</sup> 40% of the structures in the new generation are randomly generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for the structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating  $1000 \sim 1500$  structures (e.g., about  $20 \sim 30$  generations).

In order to further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform a structural optimization using density functional theory with the generalized gradient approximation<sup>4</sup> as implemented in the VASP code. In all calculations, the cutoff energy for the expansion of wavefunctions in plane waves is set to 800 eV, and the Monkhorst-Pack k-meshes<sup>5</sup> with a grid spacing of 0.189 Å<sup>-1</sup> are selected to meet the energy convergence. The electron-ion interaction is described by projector-augmented-wave potentials with the  $1s^1$ ,  $5s^25p^66s^25d^5$ , and  $3s^23p^64s^1$  configurations treated as valence electrons for H, Re, and K, respectively.

Bonding is investigated by the crystal orbital Hamiltonian population (COHP)<sup>6</sup> analysis using LOBSTER code,<sup>7</sup> which provides an atom-specific measure of the bonding character of states in a given energy region. The Bader charge analysis<sup>8</sup> is used to determine charge transfer, and the electron localization function (ELF)<sup>9</sup> is used to describe and visualize chemical bonds in molecules and solids. The phonon calculations are carried out by using supercell approach<sup>10</sup> as implemental in the PHONOPY code.<sup>11</sup> The electron-phonon coupling (EPC) calculations are performed within PWscf (Plane-Wave Self-Consistent Field) package in QUANTUM ESPRESSO.<sup>12</sup> We employ ultrasoft pseudopotentials of K.pbe-spn-rrkjus psl.1.0.0.UPF, Re.pbe-spn-rrkjus psl.1.0.0.UPF, and H.pbe-rrkjus psl.1.0.0.UPF, respectively. An energy cutoff for wave-function expansion 70 Ry is adopted to ensure enthalpy convergence (0.01 eV/atom) with a Gaussian width of 0.02 Ry. The  $2 \times 6 \times 3$  and  $4 \times 4 \times 3$  q-point meshes in the first Brillouin zone were used in the EPC calculation for the *Pmma* and *P6*<sub>3</sub>/*mmc* phases, respectively. Correspondingly, Monkhorst-Pack grids of  $4 \times 12 \times 9$ and  $8 \times 8 \times 6$  are used to ensure k-point sampling convergence. We employ the double-delta smearing technique in ph.x, and smearing width (el ph sigma) is 0.005. When EPC parameter  $\lambda$  $\leq$ 1.5, the *T*<sub>c</sub> is estimated from the McMillan-Allen-Dynes formula

$$T_{c} = \frac{\omega_{log}}{1.2} exp^{[10]} \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^{*}(1 + 0.62\lambda)} \right]$$

When the EPC parameter  $\lambda > 1.5$ , the Allen-Dynes modified McMillan equation needs to be corrected further by considering two separate correction factors ( $f_1$  and  $f_2$ ),

$$T_{c} = \frac{f_{1}f_{2}\omega_{log}}{1.2}exp^{[to]} \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^{*}(1+0.62\lambda)} \right]$$

Here, the  $\mu^*$  is the Coulomb pseudopotential and used to describe the interaction between electrons ( $\mu^* = 0.1$ ). In addition, the EPC constant,  $\lambda$ , and the logarithmic average phonon frequency,  $\omega_{\log}$  are calculated via the Eliashberg spectral function for electron-phonon interaction:

$$\alpha^{2}F(\omega) = \frac{1}{N(E_{F})}\sum_{kq,\nu}|g_{k,k+q,\nu}|^{2}\delta(\varepsilon_{k})\delta(\varepsilon_{k+q})\delta(\omega-\omega_{q,\nu})$$
where  $\lambda = 2\int d\omega \frac{\alpha^{2}F(\omega)}{\omega}$ ;  $\omega_{log} = exp\left[\frac{2}{\lambda}\int \frac{d\omega}{\omega}\alpha^{2}F(\omega)\ln^{\frac{1}{10}}(\omega)\right]$ ;  $f_{1} = \left[1 + \left[\frac{\lambda}{2.46(1+3.8\mu^{*})}\right]^{\frac{3}{2}}\right]^{\frac{1}{3}}$ 

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$$f_{2} = 1 + \frac{\left(\frac{\omega_{2}}{\omega_{log}} - 1\right)\lambda^{2}}{\lambda^{2} + \left[1.82(1 + 6.3\mu^{*})\left(\frac{\bar{\omega}_{2}}{\omega_{log}}\right)\right]^{2}}; \quad \bar{\omega}_{2} = \left[\frac{2}{\bar{\lambda}}\int d\omega \alpha^{2}F(\omega)\omega\right]^{\frac{1}{2}}. \text{ Here, } N(E_{F}) \text{ is the electronic}$$

DOS at the  $E_F$ ,  $\omega_{q,v}$  is the phonon frequency of mode v and wave vector q, and  $|g_{k, k+q, v}|$  is the electron-phonon matrix element between two electronic states with momenta k and k + q at the  $E_F$ .<sup>13</sup>



## **Supplemental Figures**

Figure S1. Phonon spectra of the three high-pressure K<sub>2</sub>ReH<sub>9</sub> phases: (a-d) *Pma*2 at 40, 50, 60, and 75 GPa, (e-i) *Pmma* at 60, 75, 100, 200, and 225 GPa, and (j-n)  $P6_3/mcm$  at 40, 50, 175, 210, and 225 GPa. And the dynamic stability intervals are 50-75 GPa for *Pma*2, 75-200 GPa for *Pmma*, and 50-210 GPa for  $P6_3/mcm$ .



Figure S2. The local configurations of (a) P-62m K<sub>2</sub>ReH<sub>9</sub>, (b) Pma2 K<sub>2</sub>ReH<sub>9</sub>, (c) Pmma K<sub>2</sub>ReH<sub>9</sub>, and

(d) P6<sub>3</sub>/mcm K<sub>2</sub>ReH<sub>9</sub>.



Figure S3. The calculated crystal orbital Hamiltonian populations (COHP) for (a) Re-H1, and (b) H1–H1 pairs in Pma2 K<sub>2</sub>ReH<sub>9</sub>, Pmma K<sub>2</sub>ReH<sub>9</sub>, and  $P6_3/mcm$  K<sub>2</sub>ReH<sub>9</sub>.



Figure S4. The ELF isosurface for (a) Pma2 K<sub>2</sub>ReH<sub>9</sub>, (b) Pmma K<sub>2</sub>ReH<sub>9</sub>, and (c) P6<sub>3</sub>/mcm K<sub>2</sub>ReH<sub>9</sub>.



Figure S5. The calculated electronic band structures of (a) *Pma2* at 50 GPa, (b) *Pmma* at 100 GPa, and (c)  $P6_3/mcm$  at 175 GPa. PDOS of (d) *Pma2* at 50 GPa, (e) *Pmma* at 100 GPa, and (f)  $P6_3/mcm$  at 175 GPa.



Figure S6. (a-e) Fermi surfaces of *Pmma* K<sub>2</sub>ReH<sub>9</sub> at 100 GPa. (f) Merged five Fermi surfaces. (g) 2D Fermi surface contours at  $k_x = 0$ .



Figure S7. (a) The projected electronic band structure, (b) phonon dispersion curves projected with the weight of EPC parameter  $\lambda$ , and (c) the projected phonon density of states and Eliashberg spectral function of *Pmma* K<sub>2</sub>ReH<sub>9</sub> at 100 GPa.



Figure S8. (a-d) Fermi surfaces of  $P6_3/mcm$  K<sub>2</sub>ReH<sub>9</sub> at 175 GPa. (e) Merged four Fermi surfaces. (f) 2D Fermi surface contours at  $k_x = 0$ .



Figure S9. The calculated phonon dispersion curves of  $P6_3/mcm$  K<sub>2</sub>ReH<sub>9</sub> at (a) 75, (b) 100, (c) 125, (d) 150, (e) 175, and (f) 200 GPa.



Figure S10. The PDOS evolution of the atom with pressure. With the contribution of decreasing pressure to Fermi level, (a) K atom decreases gradually, (b) Re atom remains constant, (c) H1 atom increases, (d) H2 atom also tends to increase.



Figure S11. The calculated ELF of  $P6_3/mcm$  K<sub>2</sub>ReH<sub>9</sub> at (a) 75, (b) 100, (c) 125, (d) 150, (e) 175, and (f) 200 GPa.



Figure S12. PDOS of H1 atom in H-H covalent bond of *Pmma* and  $P6_3/mcm$  phases at (a) 100 GPa and (b) 175 GPa.

### **Supplemental Tables**

Space group	Pressure (GPa)	K	Re	H1	H2
Pma2	50	+0.671	+0.874	-0.078	-0.294
Pmma	100	+0.591	+0.904	-0.117	-0.265
<i>P</i> 6 <sub>3</sub> / <i>mcm</i>	175	+0.499	+0.922	-0.214	-0.213

**Table S1.** Bader charge analysis of the three high-pressure K<sub>2</sub>ReH<sub>9</sub> phases. Positive values represent losing electron, and negative values represent gaining electron (unit: e<sup>-</sup>).

**Table S2.** Bader charge analysis of  $P6_3/mcm$  K<sub>2</sub>ReH<sub>9</sub> at different pressures. Positive values represent losing electron, and negative values represent gaining electron (unit: e<sup>-</sup>). The average gaining electrons of H1 and H2 atoms are denoted as H<sub>average</sub>.

Pressure (GPa)	ssure (GPa) K		H1	H2	H <sub>average</sub>
75	+0.596	+1.011	-0.264	-0.206	-0.245
100	+0.568	+0.981	-0.248	-0.210	-0.235
125	+0.543	+0.957	-0.234	-0.212	-0.227
150	+0.520	+0.937	-0.223	-0.213	-0.220
175	+0.499	+0.922	-0.214	-0.213	-0.213
200	+0.480	+0.911	-0.207	-0.210	-0.208

**Table S3.** The calculated critical temperature  $T_c$  ( $\mu^* = 0.1$ ) from McMillan-Allen-Dynes formula, EPC parameter ( $\lambda$ ), phonon frequency logarithmic average ( $\omega_{log}$ ) and the electronic DOS at Fermi level  ${}^{N_{E_F}}$  (unit: Ry) for *Pmma* and *P6*<sub>3</sub>/*mcm* K<sub>2</sub>ReH<sub>9</sub> at different pressures, respectively.

Space group	Pressure (GPa)	λ	$\omega_{\log}(\mathrm{K})$	$T_{\rm c}({\rm K})$	$N_{E\!f}$
Pmma	100	0.59	440.33	9.6	8.83
	175	0.73	1064.05	40.6	10.94
<i>P</i> 6 <sub>3</sub> / <i>mcm</i>	75	2.06	702.69	127.1	13.35
	100	1.64	857.64	122.1	13.11
	125	1.28	1020.39	98.6	12.84

150	1.04	1143.65	84.5	12.60
175	0.90	1212.77	70.6	12.38
200	0.81	1239.11	59.9	12.20

Table S4. Structural information of the three predicted K<sub>2</sub>ReH<sub>9</sub> phases.

Space group	Pressure (GPa)	Lattice Parameters (Å)	Atomic positions			
Pma2			K(4d)	-0.9277	0.2610	0.0062
		a = 9.0270	Re(2c)	-0.2500	0.2437	0.5413
		b = 5.3707	H1(4d)	-0.4040	0.4240	0.5088
	50	c = 2.8827	H2(4d)	-0.6543	0.8665	0.9844
	30		H3(4d)	-1.0963	0.0574	0.4923
		$\alpha = \beta = \gamma = 90^{\circ}$	H4(2c)	-0.7500	0.3231	0.5024
			H5(2c)	-0.2500	0.8258	0.5080
			H6(2c)	-0.2500	0.4444	0.9842
	100		K(4i)	1.4237	0.0000	0.7389
		a = 8.4538	Re(2f)	1.2500	0.5000	0.2425
Pmma		u = 0. <b>-</b> 556	H1(4i)	1.3491	0.0000	0.1305
		b = 2.7824	H2(4j)	0.5840	0.5000	0.5757
		c = 4.8952	H3(2f)	1.2500	0.5000	0.8402
		0 110902	H4(2f)	0.7500	0.5000	0.3375
		$\alpha = \beta = \gamma = 90^{\circ}$	H5(4j)	1.0759	0.5000	0.0568
			H6(2e)	1.2500	0.0000	0.4499
P6 <sub>3</sub> /mcm	175	a = b = 4.5018				
		<i>c</i> = 5.5525	K(4c)	0.6667	0.3333	1.2500
		$\alpha = \beta = 90^{\circ}$	Re(2b)	0.0000	0.0000	0.5000
			H1(12k)	0.3758	1.0000	0.9967
		$\gamma = 120^{\circ}$	H2(6g)	0.7934	0.7934	1.2500

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