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Supplementary Material

High-temperature superconductivity in transition metallic hydrides MH_{11} (M=Mo, W, Nb, Ta) under high pressure

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FIGURES

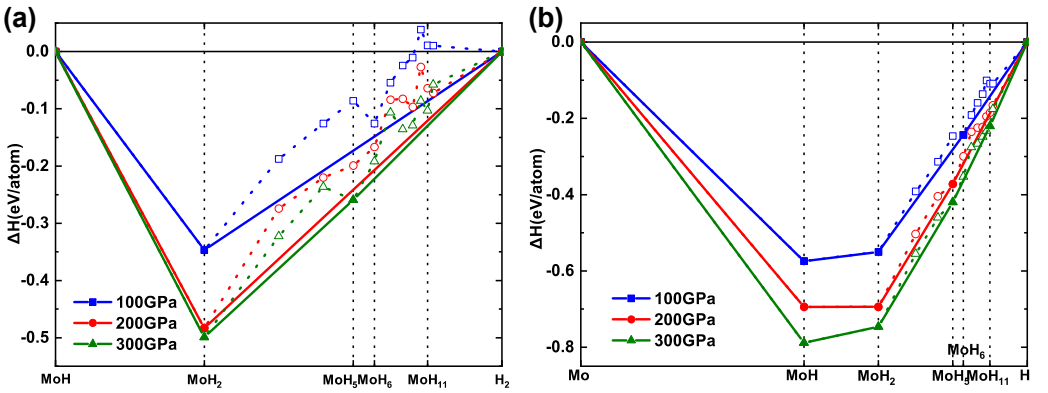


Fig. S1 (a) The convex hull of the Mo–H system relative to MoH and H_2 at 100, 200, 300 GPa without zero-point energy. (b) The convex hull of the Mo–H system relative to Mo[1] and H_2 at 100, 200, 300 GPa with zero-point energy.

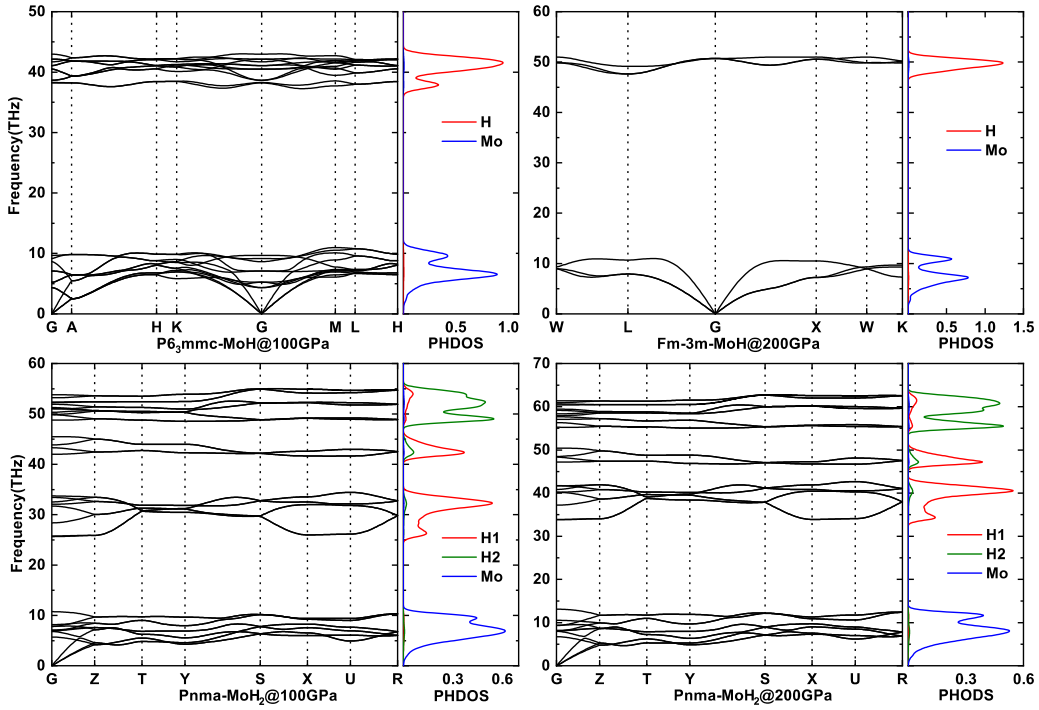


Fig. S2 The phonon band structure and PHDOS of MoH and MoH_2 at different pressures.

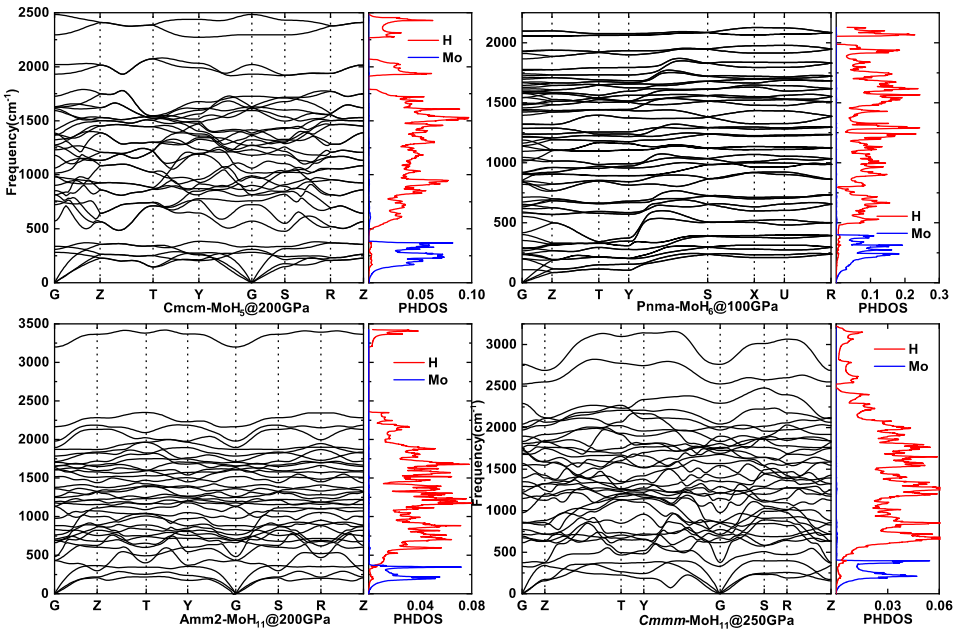


Fig. S3 The phonon band structure and PHDOS of MoH_5, MoH_6 and MoH_{11} at different pressures.

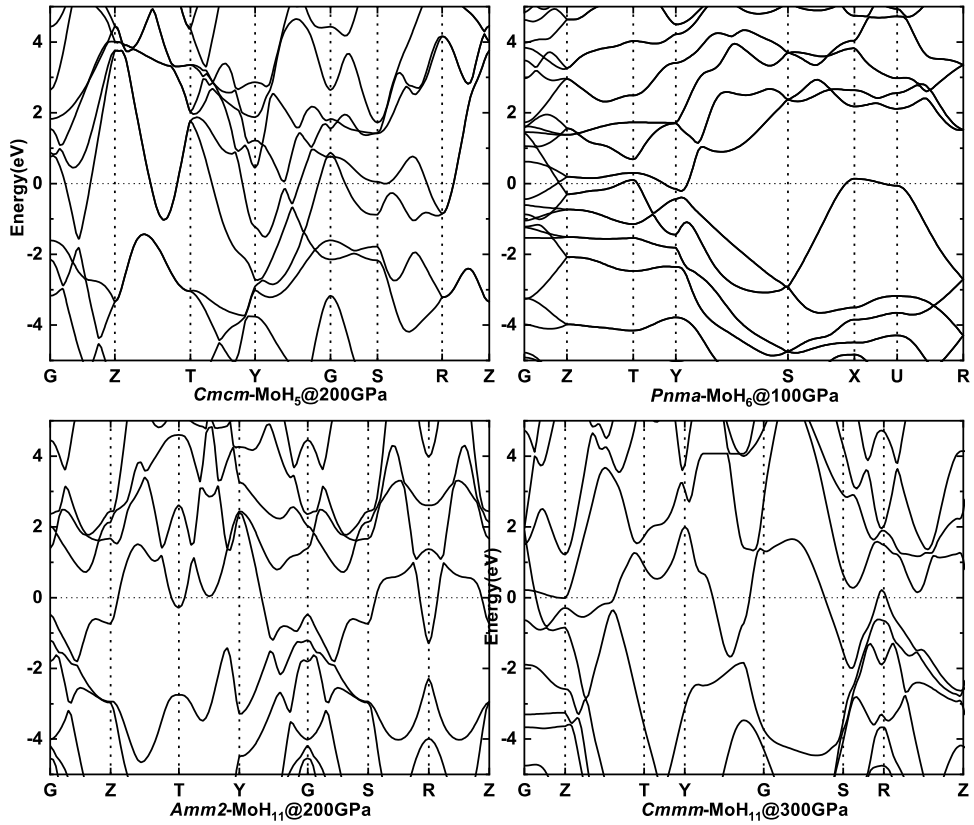


Fig. S4 The electronic band structures of MoH_5, MoH_6 and MoH_{11}.

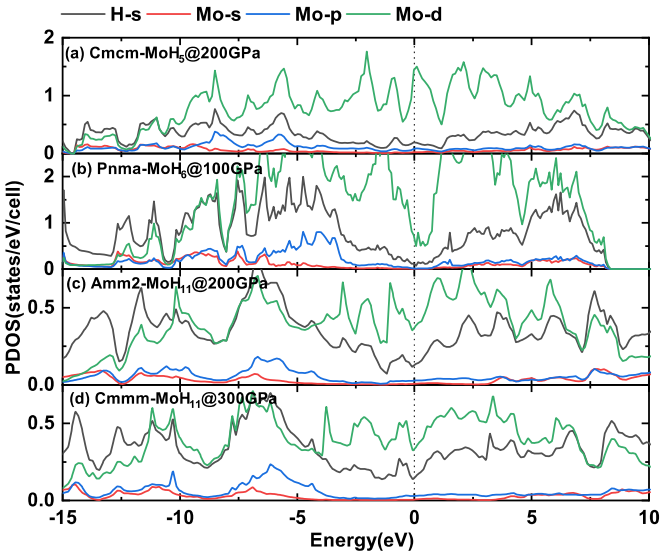


Fig. S5 The projected density of states of MoH_5, MoH_6 and MoH_{11}.

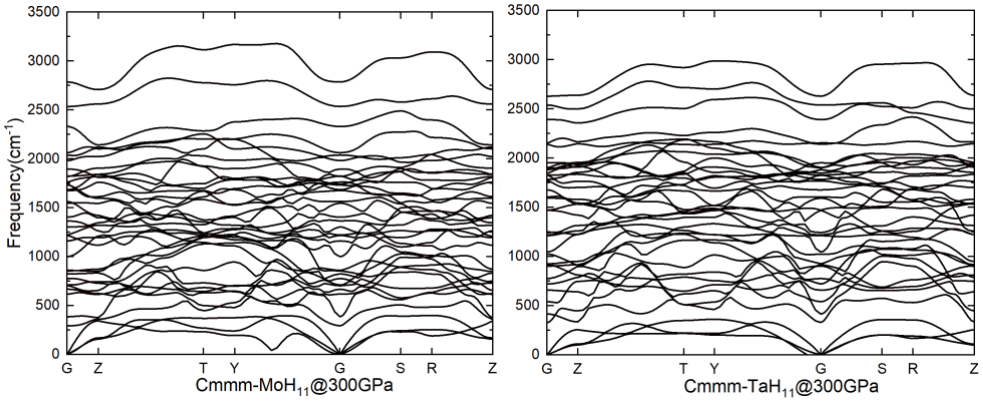


Fig. S6 The phonon band structure of MoH_{11} and TaH_{11}.

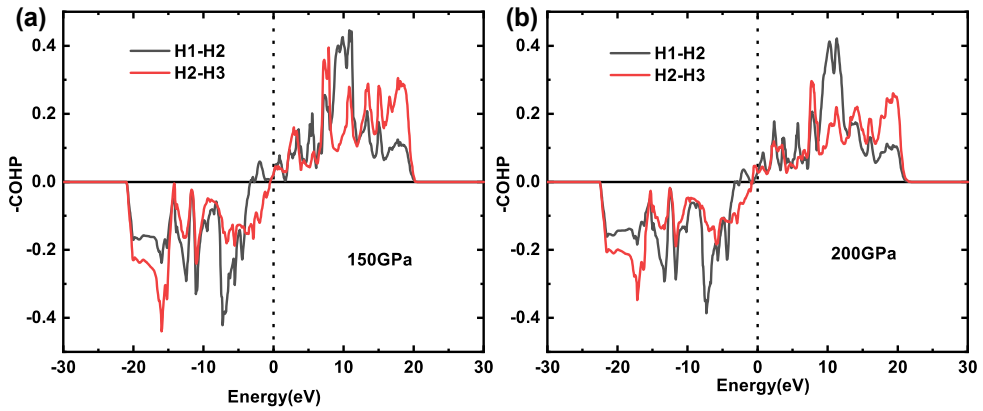


Fig. S7 Crystal orbital Hamilton population (COHP) of H1-H2, and H2-H3 in *Amm2*-MoH_{11} at (a) 150GPa and (b) 200GPa.

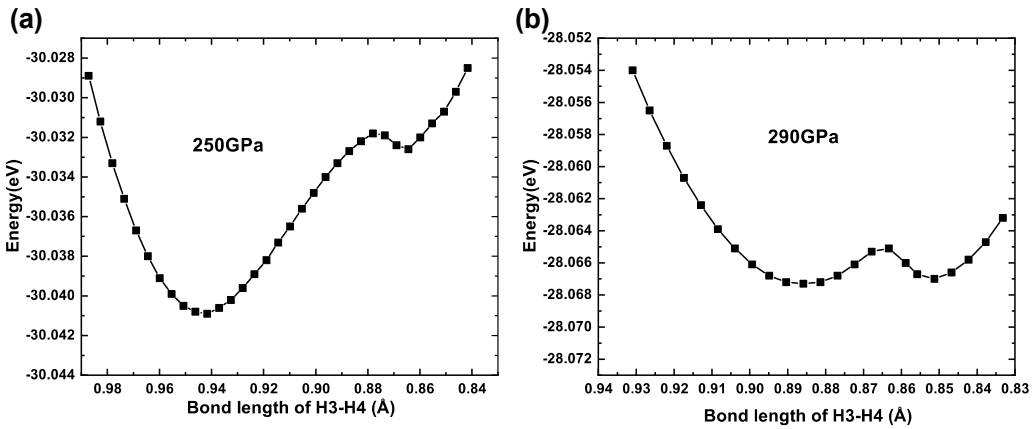


Fig. S8 The total energy of Amm2-Cmmm phase transition at (a) 250GPa and (b) 290GPa.

TABLES

Table S1 Lattice parameters and atomic positions of MoH, MoH_2, MoH_5, MoH_6 and MoH_{11}.

Structure	Parameters (Å, deg)	Atom	x	y	z
P6₃/mmc MoH (100 GPa)	a=b=2.70290 c=4.41530	H Mo	0.00000 0.33333	0.00000 0.66667	0.00000 0.25000
Fm-3m MoH (100 GPa)	a=b=c=3.81860	H Mo	0.50000 0.00000	0.50000 0.00000	-0.50000 0.00000
Pnma MoH_2 (100 GPa)	a=4.51460 b=2.83170 c=4.95570	H H Mo	0.48495 -0.37410 -0.23585	0.75000 0.25000 0.75000	0.78365 0.57557 0.41310
Cmcm MoH_5 (200 GPa)	a=4.57980 b=6.13100 c=2.66890	H H H Mo	0.64033 0.78877 0.50000 0.50000	0.12905 0.06005 -0.04449 -0.30813	0.75000 1.25000 0.75000 0.75000
Pnma MoH_6 (100 GPa)	a=4.76530 b=2.81750 c=7.41910	H H H H H H Mo	0.99926 0.57195 0.61171 0.88123 0.75075 0.18183 0.37583	0.25000 0.25000 0.25000 0.25000 0.75000 0.75000 0.25000	0.12876 0.72288 0.51024 0.60061 0.64366 0.07088 0.13906
Amm2 MoH_{11} (200 GPa)	a=4.53180 b=2.74420 c=4.64280	H H H H H H H H Mo	0.20170 0.20005 0.62854 0.63653 0.50000 0.50000 0.50000 0.50000 0.00000	0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000	-0.89077 -0.18830 -0.43667 -0.65084 -0.81994 -0.03556 -0.20437 -0.50951
Cmmm MoH_{11} (300 GPa)	a=4.51360 b=2.58370 c=4.37040	H H H H Mo	0.15572 -0.39151 0.18947 0.00000 0.00000	0.50000 0.50000 0.50000 0.50000 0.00000	0.78513 0.62775 0.50000 0.50000 0.00000

Table S2 Remnant Charges on H and Mo Atoms Obtained from Bader Charge Analysis of MoH, MoH_2, MoH_5, MoH_6 and MoH_{11}.

Structure	**Atom**	**charge**	**σ (e)**
P6₃/mmc MoH	H	1.3888	-0.3888
(100 GPa)	Mo	5.6112	0.3888
Fm-3*m* MoH	H	1.3892	-0.3892
(100 GPa)	Mo	5.6108	0.3892
Pnma MoH_2	H	1.3237	-0.3237
(100 GPa)	H	1.3566	-0.3566
	Mo	5.3197	0.6803
Cmcm MoH_5	H	1.1758	-0.1758
(200 GPa)	H	1.1790	-0.1790
	H	1.1598	-0.1598
	H	1.1398	-0.1398
	Mo	5.1857	0.8143
Pnma MoH_6	H	1.0629	-0.0629
(100 GPa)	H	1.1758	-0.1758
	H	1.1149	-0.1149
	H	1.1827	-0.1827
	H	1.0629	-0.0629
	H	1.1902	-0.1902
	H	1.1899	-0.1899
	Mo	5.0836	0.9164
Amm2 MoH_{11}	H	1.1392	-0.1392
(200 GPa)	H	1.1289	-0.1289
	H	1.1398	-0.1398
	H	1.0149	-0.0149
	H	1.0745	-0.0745
	H	0.9701	0.0299
	H	1.0665	-0.0665
	H	1.0820	-0.0820
	Mo	5.1458	0.8542
Cmmm MoH_{11}	H	1.1417	-0.1417
(300 GPa)	H	1.0215	-0.0215
	H	1.1038	-0.1038
	H	1.1459	-0.1459
	H	1.0323	-0.0323
	H	0.9935	0.0065
	Mo	5.1162	0.8838

σ represents the charge transferred from Mo to H.

Table S3. The calculated EPC parameter (λ), logarithmic average phonon frequency (ω_{log}), electron density of states at the Fermi level (N_{Ef}, states/spin/Ry/Cell), superconducting critical temperature T_c and $f_1f_2T_c$ using Allen-Dynes modified McMillan equation.

Phase	Pressure (GPa)	λ	ω_{log} (K)	N_{Ef}	T_c (K)	$f_1f_2T_c$ (K)
Cmcm-MoH_5	150	1.68	577	10.75	67-72	77-86
	200	1.45	729	10.15	73-80	82-91
	250	1.36	824	9.73	77-85	85-96
	300	1.34	880	9.40	80-89	88-100
Pnma-MoH_6	100	0.86	503	9.44	22-27	24-29
Amm2-MoH_{11}	200	1.59	794	5.93	87-95	100-111
	250	1.75	861	6.38	103-112	121-134
Cmmm-MoH_{11}	250	1.54	1004	6.11	107-117	121-135

the Coulomb pseudopotential $\mu^* = 0.10$ and 0.13.

Table S4. The calculated EPC parameter (λ), logarithmic average phonon frequency (ω_{log}), electron density of states at the Fermi level (N_{Ef}, states/spin/Ry/Cell), the contribution of H atoms DOS to the total DOS at the Fermi energy (P_H), superconducting critical temperature T_c and $f_1f_2T_c$ using Allen-Dynes modified McMillan equation and T_c^{scE} using the Self-consistent solution of the Eliashberg equation.

Phase	Pressure (GPa)	λ	ω_{log} (K)	N_{Ef}	P_H(%)	T_c (K)	$f_1f_2T_c$ (K)	T_c^{scE} (K)
Cmmm-MoH_{11}	300	1.52	1002	5.96	24.5	105-115	118-132	134-148
Cmmm-WH_{11}	300	1.57	957	5.80	28.6	106-116	121-135	135-151
Cmmm-NbH_{11}	300	1.09	1280	5.23	22.8	89-102	96-111	101-116
Cmmm-TaH_{11}	300	1.18	1257	5.02	28.7	91-104	99-114	107-122

the Coulomb pseudopotential $\mu^* = 0.10$ and 0.13.

Table S5. The strength of the interaction of electrons with optical phonons λ_{opt} and acoustic phonons λ_{ac} for each of these regions and the corresponding average frequencies ω_{opt} and ω_{ac}, isotope coefficients α, the critical temperature upon the substitution of deuterium for hydrogen T_c^D and T_c^{GK} calculated by the G-K equation.

Phase	Pressure (GPa)	λ_{opt}	λ_{ac}	Ω_{opt}	Ω_{ac}	α	T_c^D	T_c^{GK}(K)
Cmmm-MoH_{11}	300	1.09	0.4	1949	347	0.36	124-137	160-177
Cmmm-WH_{11}	300	1.19	0.36	1820	280	0.39	116-129	152-168
Cmmm-NbH_{11}	300	0.85	0.24	2128	472	0.39	89-104	117-137
Cmmm-TaH_{11}	300	0.91	0.21	2102	386	0.41	91-105	121-139

the Coulomb pseudopotential $\mu^* = 0.10$ and 0.13.

Equations for calculating T_c and related parameters

(1) Gor'kov-Kresin equation

In the study of hydrides, in order to explore the behavior of hydrogen atoms, Lev P. Gor'kov and Vladimir Z. Kresin divided the electroacoustic interaction into two parts according to the acoustic branch and the optical branch[2]:

$$\lambda_{ac} = 2\int_0^{\omega_1} \frac{\alpha^2 F(\omega)}{\omega} d\omega \tag{1}$$

$$\lambda_{opt} = 2\int_{\omega_1}^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega \tag{2}$$

$$\langle {\omega_{ac}}^2 \rangle = \frac{2}{\lambda_{ac}} \int_0^{\omega_1} d\omega \cdot \omega^2 \frac{\alpha^2 F(\omega)}{\omega} = \frac{2}{\lambda_{ac}} \int_0^{\omega_1} \alpha^2 F(\omega) \omega d\omega \tag{3}$$

$$\langle {\omega_{opt}}^2 \rangle = \frac{2}{\lambda_{opt}} \int_{\omega_1}^{\infty} d\omega \cdot \omega^2 \frac{\alpha^2 F(\omega)}{\omega} = \frac{2}{\lambda_{opt}} \int_0^{\omega_1} \alpha^2 F(\omega) \omega d\omega \tag{4}$$

T_c is written as

$$T_c = T_c^{opt} + \Delta T_c^{ac} \tag{5}$$

$$T_c^0 \equiv T_c^{opt} \tag{6}$$

When $\lambda_{ac} \ll \lambda_{opt}$, we can obtain the following analytical expression for the critical temperature of the high-T_c phase:

$$T_c = \left[1 + 2\frac{\lambda_{ac}}{\lambda_{opt} - \mu^*} \cdot \frac{1}{1+\eta^{-2}}\right] T_c^0 \tag{7}$$

$$\eta = \frac{\widetilde{\omega}_{ac}}{\pi T_c^0} \tag{8}$$

When $\lambda_{opt} \leq 1.5$, we can use the McMillan-Dynes expression for T_c^0:

$$T_c^0 = \frac{\widetilde{\omega}_{opt}}{1.2} exp\left[-\frac{1.04(1+\lambda_{opt})}{\lambda_{opt} - \mu^*(1+0.62\lambda_{opt})}\right] \tag{9}$$

When $\lambda_{opt} > 1.5$, another option is to use the analytical expression, valid for any value of the coupling constant:

$$T_c^0 = \frac{0.25\widetilde{\omega}_{opt}}{\left[e^{\frac{2}{\lambda_{eff}}} - 1\right]^{\frac{1}{2}}} \tag{10}$$

$$\lambda_{eff} = (\lambda_{opt} - \mu^*)\left[1 + 2\mu^* + \lambda_{opt}\mu^* t(\lambda_{opt})\right]^{-1} \tag{11}$$

$$t(x) = 1.5\exp(-0.28x) \tag{12}$$

In the case $T_c < \widetilde{\omega}_{ac} \ll \widetilde{\omega}_{opt}$, one can estimate T_c with:

$$T_c \approx {\widetilde{\omega}_{opt}}^{\frac{\lambda_{opt}}{\lambda}} {\widetilde{\omega}_{ac}}^{\frac{\lambda_{ac}}{\lambda}} exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right) \tag{13}$$

The value of the isotope coefficient α in the high-T_c phase can be calculated with the use of

$$\alpha = \frac{1}{2}\left[1 - 4\frac{\lambda_{ac}}{\lambda_{opt}} \frac{\eta^2}{(\eta^2+1)^2}\right] \tag{14}$$

The critical temperature value after isotope replacement T_c^D can be calculated by

$$\frac{T_c}{T_c^D} = \left(\frac{M_H}{M_D}\right)^{-\alpha} \tag{15}$$

(2) The Allen−Dynes-modified McMillan equation

T_c can be estimated by the McMillan equation[3]:

$$T_c = \frac{\omega_{log}}{1.2} exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \tag{16}$$

where λ and ω_{log} are the electron−phonon coupling constant and the logarithmic-averaged phonon frequency, respectively, and μ^* is the Coulomb pseudopotential, for which we use the widely accepted range of 0.1-0.13. λ and ω_{log} are given by

$$\lambda = 2\int_0^\infty \frac{\alpha^2F(\omega)}{\omega} d\omega \tag{17}$$

and

$$\omega_{log} = exp\left(\frac{2}{\lambda}\int_0^\infty \frac{d\omega}{\omega}\alpha^2F(\omega)\, ln\,\omega\right) \tag{18}$$

The parameter ω denotes the phonon frequency, and $\alpha^2F(\omega)$ is the Eliashberg spectral function

$$\alpha^2F(\omega) = \frac{1}{2\pi N(\varepsilon_F)}\sum_{\boldsymbol{q}\upsilon}\frac{\gamma_{\boldsymbol{q}\upsilon}}{\omega_{\boldsymbol{q}\upsilon}}\delta(\omega-\omega_{\boldsymbol{q}\upsilon}) \tag{19}$$

The line width $\gamma_{q,\upsilon}$ is written as

$$\gamma_{q\upsilon} = \pi\omega_{q\upsilon}\sum_{mn}\sum_k |g^{\upsilon}_{mn}(\boldsymbol{k},\boldsymbol{q})|^2\,\delta(\varepsilon_{m,\boldsymbol{k}+\boldsymbol{q}}-\varepsilon_F)\times\delta(\varepsilon_{n,\boldsymbol{k}}-\varepsilon_F) \tag{20}$$

where $\varepsilon_{n,\mathbf{k}}$ is the energy of the bare electronic Bloch state, ε_F is the Fermi energy, and $g^{\upsilon}_{mn}(\boldsymbol{k},\boldsymbol{q})$ is the electron−phonon matrix element.

When the value of λ larger than 1.3, strong-coupling corrections begin to appear. Therefore, P. B. Allen and R. C. Dynes use two separate correction factors (f_1 and f_2) to describe these two effects. Then we can further obtain the Allen−Dynes-modified McMillan equation[4]:

$$T_c = \frac{f_1 f_2\omega_{log}}{1.2} exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] \tag{21}$$

f_1 and f_2 are given by

$$f_1 = \sqrt[3]{\left[1+\left(\frac{\lambda}{2.46(1+3.8\mu^*)}\right)^{\frac{3}{2}}\right]} \tag{22}$$

and

$$f_2 = 1+\frac{\left(\frac{\omega_2}{\omega_{log}}-1\right)\lambda^2}{\lambda^2+\left[1.82(1+6.3\mu^*)\frac{\bar{\omega}_2}{\omega_{log}}\right]} \tag{23}$$

average frequencies $\bar{\omega}_2$ is given by

$$\bar{\omega}_2 = \sqrt{\frac{2}{\lambda}\int_0^\infty \frac{d\omega}{\omega}\alpha^2F(\omega)\omega d\omega} \tag{24}$$

(3) Self-consistent solution of the Eliashberg equation

For strong-coupling system, it can be better described with Eliashberg equation[5]:

$$Z(i\omega_n)\Delta(i\omega_n) = \frac{\pi T}{N_F}\sum_{n'} \frac{\Delta(i\omega_n')}{\sqrt{\omega_n'^2+\Delta^2(i\omega_n')}} \times [\lambda(\omega_n - \omega_{n'}) - N_F\mu^*]\delta(\epsilon) \quad (25)$$

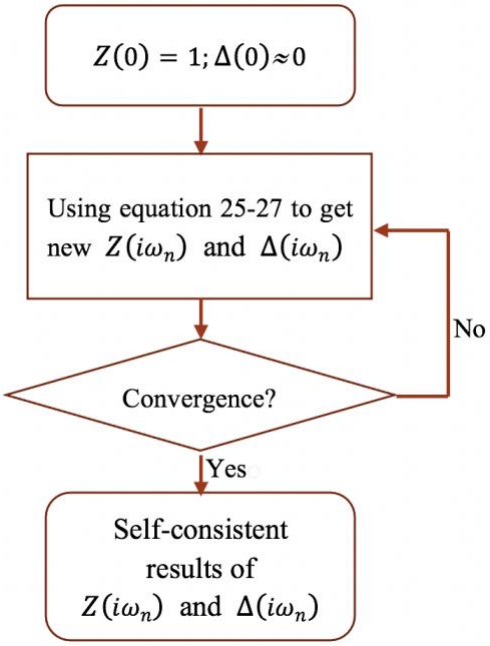
$$Z(i\omega_n) = 1 + \frac{\pi T}{N_F\omega_n}\sum_{n'} \frac{\omega_n'}{\sqrt{\omega_n'^2+\Delta^2(i\omega_n')}} \lambda(\omega_n - \omega_{n'})\delta(\epsilon) \quad (26)$$

where functions $Z(i\omega_n)$ and $\Delta(i\omega_n)$ are the renormalization function and pairing order parameter, respectively. N_F is the density of electronic states at the Fermi level, and $\delta(\epsilon)$ is the Dirac delta function. $i\omega_n = i(2n+1)\pi T_c$ are the fermion Matsubara frequencies. μ^* is the Coulomb pseudopotential, for which we use the widely accepted range of 0.1-0.13. $\lambda(\omega_n - \omega_{n'})$ contains the electron-phonon coupling matrix, phonon propagator, and the phonon density of states, and is given by:

$$\lambda(\omega_n - \omega_{n'}) = \int_0^\infty d\omega \frac{2\omega}{(\omega_n-\omega_n')^2+\omega^2}\alpha^2F(\omega) \quad (27)$$

The equations for the $Z(i\omega_n)$ and $\Delta(i\omega_n)$ form a coupled nonlinear system and are solved self-consistently. We evaluated renormalization function and the order parameter for each Matsubara frequency along the imaginary energy axis. After calculating $Z(i\omega_n)$ and $\Delta(i\omega_n)$, an analytic continuation is performed to the real axis using Pade' functions.

The specific process is as follows:



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