

Supporting Information

Novel Strongly Correlated Europium Superhydrides

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Methods

Experiment

To investigate the formation of new chemical compounds in the Eu–H system, we purchased the europium foil with 99.99% purity from Alfa Aesar company. Two diamond anvil cells (DACs) with 100 and 150 μm culets were loaded with Eu and ammonia borane (AB), purified by sublimation, which was used as a source of hydrogen and a pressure transmitting medium (Table S1). As has been shown earlier in the synthesis of superhydrides of lanthanum,¹ thorium,² praseodymium,³ and neodymium,⁴ ammonia borane is an effective source of hydrogen when the metal target is heated by a short (< 0.2 s) laser pulse due to the well-known thermal decomposition reaction: $\text{NH}_3\text{BH}_3 \rightarrow \text{H}_2 + \text{poly}(\text{BNH}_x)_n$.^{5,6}

A tungsten plate with a thickness of 20 ± 2 μm was used as a gasket. The pressure was determined by the Raman signal of diamond.⁷ Heating was carried out by pulses of an infrared laser (1 μm , Nd:YAG). A part of the X-ray diffraction (XRD) patterns of all samples studied in diamond anvil cells were recorded on 4W2 beamline of the Beijing Synchrotron Research Facilities (BSRF, China) and BL15U1 synchrotron beamline at the Shanghai Synchrotron Research Facility (SSRF, China)⁸ using a focused (5×12 μm) monochromatic X-ray beam (20 keV, 0.6199 \AA). The other part of the high-pressure XRD patterns were obtained at BL10XU in SPring-8 using monochromatic synchrotron radiation and an imaging plate detector at room temperature.⁹ The X-ray beam with a wavelength of 0.413 \AA was focused with a polymer compound refractive lens (SU-8, produced by ANKA). The experimental X-ray diffraction images were analyzed and integrated using Dioptas software package.¹⁰ The full profile analysis of the diffraction patterns and calculations of the unit cell parameters were performed in JANA2006¹¹ using the Le Bail method.¹² Additional parameters of high-pressure diamond anvil cells are listed in Table S1.

Table S1. Experimental parameters of the DACs used to synthesize europium hydrides.

Cell	Synthesis pressure, GPa	Culet size, μm	Sample size, μm	Composition/load
E1	110	100	15	Eu/BH ₃ NH ₃
E2	74	150	20	Eu/BH ₃ NH ₃
E3	86	100	13	Eu/BH ₃ NH ₃

Theory

All calculations of crystalline systems were carried out using the Vienna Ab initio Simulation Package (VASP) code^{13–15} with PAW^{16–18} pseudopotentials. The calculations were performed solely for producing the wave functions of the systems. The generalized gradient approximation (GGA) expressed by the PBE functional was applied. The Brillouin zone was sampled using the Monkhorst–Pack method.¹⁹ Considering the different number of atoms in unit cells for different compounds, various k -grids ($5 \times 5 \times 5$ and $11 \times 11 \times 11$) were used. The energy cutoff was set to 600 eV, the partial occupancies were set using the Gaussian smearing with $\sigma = 0.1$. To find the bonding pattern of the selected clusters, the solid-state adaptive natural density partitioning (SSAdNDP)²⁰ algorithm was implemented. The SSAdNDP follows the idea of the AdNDP algorithm for molecules^{21,22} and the periodic NBO method.²³ It is based on the partitioning of the electron density (1-body density matrix) and produces the interpretation of chemical bonding in systems with translational symmetry in terms of classical lone pairs and two-center bonds, as well as multicenter delocalized bonding. The algorithm produces the number of bonding elements and their occupancy numbers (ONs). Physically, it shows how many electrons are sitting in the chosen region. For the ideal Lewis case, the ON is $2.00 |e|$. It has been shown that the chemical bonding pattern obtained with the SSAdNDP has a high correlation with features of studied materials and can give important insights into the physical and chemical properties of various solids.^{24–28} The Stuttgart RSC 1997 ECP atomic

centered basis²⁹ for actinides and Def2-TZVPP³⁰ basis for other atoms were used to represent the projected PW density. For convenience, we designate this basis set combination as Basis_1. The spillage parameter of occupied bands for this basis was no higher than 1%. For spin-polarized calculations, both spin-up (alpha) and spin-down (beta) density matrices were analyzed. The resulting bonding elements were designated as alpha and beta bonds. The occupancies of doubly occupied bonding elements for spin-polarized cases were calculated as a sum of the occupancies of alpha and beta bonding elements.

For calculations of the model clusters, the Gaussian 16 program³¹ was used. The exact geometries of the solid-state hydrides were taken for modeling the wave functions. The charges of clusters were set so as to take into account the stoichiometry of the crystals. All calculations were carried out at the PBE0/Basis_1 level of theory. The ChemCraft 1.8 software³² was used to visualize the chemical bonding patterns and geometries of the investigated hydrides.

The calculations of the electron–phonon coupling and superconducting T_C were carried out with QUANTUM ESPRESSO (QE) package³² using the density functional perturbation theory,³³ employing the plane-wave generalized gradient approximation with the Goedecker–Hartwigsen–Hutter–Teter pseudopotentials.^{34,35} In our ab initio calculations of the electron–phonon coupling (EPC) parameter λ of EuH₉, the first Brillouin zone was sampled by $2 \times 2 \times 2$ q -points mesh and $10 \times 10 \times 10$ k -points meshes with a smearing $\sigma = 0.005$ – 0.05 Ry that approximates the zero-width limits in the calculation of λ . The critical temperature T_C was calculated using the Allen–Dynes equations.³⁶

To calculate U – J , we took the most stable collinear states for each of the three phases (AFM 2 $F\bar{4}3m$ -EuH₉, FM $P6_3/mmc$ -EuH₉, and FM $Pm\bar{3}n$ -Eu₈H₄₆) and the computed DFT ground state with U – $J = 0$. Then, we computed the “bare” and “interacting” responses by applying a series of small perturbations ($\alpha = -0.08, -0.05, -0.02, 0.02, 0.05, 0.08$) to one of the Eu sites. We obtained the response functions from a linear fit of the number of f electrons on the perturbed atomic site as a function of the applied potential α (Figure S4). From the slopes of these functions we obtained the value of U – J (Table S6). The obtained results were close to those previously described in the study of $P6_3/mmc$ -NdH₉.⁴

Before starting the magnetic calculations, we checked the parameters for convergence. After several tests with different VASP pseudopotentials (Eu_2, Eu), we noticed that the computed magnetization on each atom was always zero, which is physically meaningless. The only pseudopotential which allowed us to study the magnetic properties of EuH₉ is Eu (PAW_PBE_Eu_23Dec2003, $z_{val} = 17$), so we used it together with that of H, both taken from the VASP library. The kinetic energy cutoff of the plane wave basis set was chosen to be 540 eV (520 eV) for the $F\bar{4}3m$ ($P6_3/mmc$) phase, which gives a maximum error of 1 meV/atom with respect to more accurate calculations. The same error criterion was used when choosing, for both EuH₉ phases, a length $l = 40$ for the automatic generation of GAMMA-centered Monkhorst–Pack grids as implemented in the VASP code, and a smearing parameter SIGMA = 0.2 with the Methfessel–Paxton method of order 1.

Structural Information

Table S2. Calculated (SOC, DFT+U, $U-J = 5$ eV) crystal structure of the discovered Eu–H phases.

Phase	Pressure,	Lattice	Coordinates			
$P6_3/mmc$ -EuH ₉	100	$a = 3.559 \text{ \AA}$ $c = 5.855 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	Eu1	0.33333	0.66667	0.75000
			H1	0.00000	0.00000	0.25000
			H2	0.33333	0.66667	0.33627
			H3	0.15200	0.30401	0.04717
$F\bar{4}3m$ -EuH ₉	100	$a = 5.041 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	Eu1	0.25000	0.25000	0.25000
			H1	-0.13655	-0.13655	-0.13655
			H2	-0.38097	-0.38097	-0.38097
			H3	0.00000	0.00000	0.00000
$Pm\bar{3}n$ -Eu ₄ H ₄₆	130	$a = 5.865 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	Eu1	0.00000	0.00000	0.00000
			Eu2	0.25000	0.00000	0.50000
			H1	0.00000	0.11963	0.30584
			H2	0.25000	0.50000	0.00000
			H3	0.18451	0.18451	0.18451
$Fm\bar{3}n$ -EuH ₁₀	100	$a = 5.183 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	Eu	0.00000	0.00000	0.00000
			H1	0.11916	0.11916	0.11916
			H2	0.25000	0.25000	0.25000
$P1$ -EuH ₉ (pseudo-hexagonal)	130	$a=3.5598 \text{ \AA}$ $b=6.8524 \text{ \AA}$ $c=6.1657 \text{ \AA}$ $\alpha=63.26^\circ$ $\beta=90^\circ$ $\gamma=74.94^\circ$	Eu1	0.375	0.25	0.708333
			Eu2	0.625	0.75	0.291667
			Eu3	0.875	0.25	0.208333
			Eu4	0.125	0.75	0.791667
			H1	0.625	0.75	0.625
			H2	0.125	0.75	0.125
			H3	0.875	0.25	0.875
			H4	0.375	0.25	0.375
			H5	0.918135	0.16373	0.584801
			H6	0.418135	0.16373	0.084801
			H7	0.081865	0.83627	0.415199
			H8	0.581865	0.83627	0.915199
			H9	0.168135	0.66373	0.501468
			H10	0.668135	0.66373	0.001468
			H11	0.831865	0.33627	0.498532
			H12	0.331865	0.33627	0.998532
			H13	0.501592	0.452831	0.349587
			H14	0.001592	0.452831	0.849587
			H15	0.498408	0.547169	0.650413
			H16	0.998408	0.547169	0.150413
			H17	0.773584	0.452831	0.621579
			H18	0.273584	0.452831	0.121579
			H19	0.226416	0.547169	0.378421
			H20	0.726416	0.547169	0.878421
			H21	0.045577	0.452831	0.349587
			H22	0.545577	0.452831	0.849587
			H23	0.954423	0.547169	0.650413

			H24	0.454423	0.547169	0.150413
			H25	0.295577	0.952831	0.447582
			H26	0.795577	0.952831	0.947582
			H27	0.704423	0.047169	0.552418
			H28	0.204423	0.047169	0.052418
			H29	0.023584	0.952831	0.175589
			H30	0.523584	0.952831	0.675589
			H31	0.976416	0.047169	0.82441
			H32	0.476416	0.047169	0.32441
			H33	0.751592	0.952831	0.447582
			H34	0.251592	0.952831	0.947582
			H35	0.248408	0.047169	0.552418
			H36	0.748408	0.047169	0.052418
<i>P</i> 1-EuH ₉ (pseudocubic)	130	$a=3.5646 \text{ \AA}$ $b=3.5646 \text{ \AA}$ $c=6.1742 \text{ \AA}$ $\alpha=90^\circ$ $\beta=73.22^\circ$ $\gamma=60^\circ$	Eu1	0.75	0.125	0.375
			Eu2	0.75	0.625	0.875
			H1	0.59035	0.204825	0.068275
			H2	0.59035	0.704825	0.568275
			H3	0.13655	0.658625	0.068275
			H4	0.13655	0.158625	0.568275
			H5	0.13655	0.431725	0.295175
			H6	0.13655	0.931725	0.795175
			H7	0.13655	0.204825	0.068275
			H8	0.13655	0.704825	0.568275
			H9	0.857095	0.571452	0.190484
			H10	0.857095	0.071452	0.690484
			H11	0.380968	0.047579	0.190484
			H12	0.380968	0.547579	0.690484
			H13	0.380968	0.809515	0.428548
			H14	0.380968	0.309515	0.928548
			H15	0.380968	0.571452	0.190484
			H16	0.380968	0.071452	0.690484
			H17	0.0	0.0	0.0
			H18	0.0	0.5	0.5

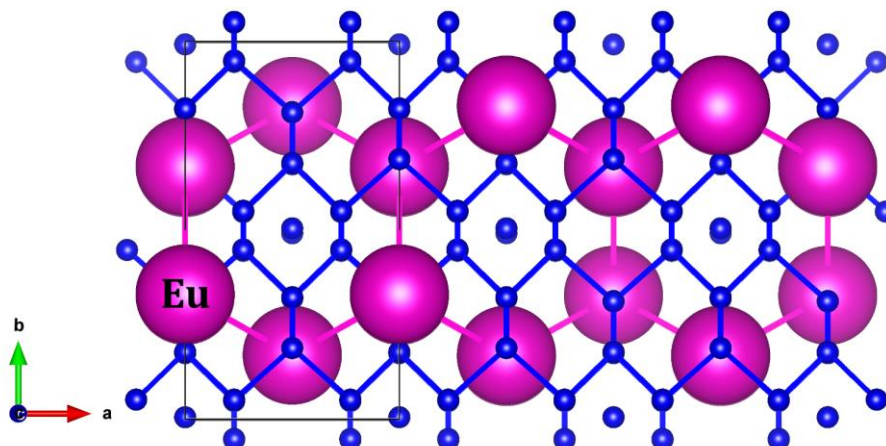


Figure S1. Crystal structure of pseudo-hexagonal *P*1(hex)-EuH₉ (=Eu₄H₃₆) with the disordered hydrogen sublattice, visualized using VESTA software.³⁷ The hydrogen atoms are shown in blue.

Table S3. Experimental and theoretical cell parameters of all studied Eu–H phases. $V_{\text{DFT+U}}$ is calculated with SOC and $U-J = 5$ eV, V_{DFT} is calculated without the Hubbard correction. Data in brackets correspond to experiment at $\lambda = 0.6199$ Å and 0.413 Å.

Compound	Pressure, GPa	a , Å	c , Å	V , Å ³ per Eu atom	$V_{\text{DFT+U}}$, Å ³ per Eu atom	V_{DFT} , Å ³ per Eu atom
$Pm\bar{3}n$ -Eu ₈ H ₄₆ ($Z = 8$)	130	5.8582		25.13	25.21	24.75
	125	5.8604		25.16	25.49	25.02
	121	5.8649		25.22	25.77	25.29
	116	5.8862		25.49	26.08	25.58
	111	5.9069 (5.9080)		25.76 (25.77)	26.38	25.88
	106	5.9492		26.32	26.65	26.15
	102	5.9547		26.39	26.92	26.38
	99	5.9656		26.54	27.13	26.58
	97	5.9729		26.63	27.26	26.71
	94	5.9732		26.64	27.54	26.96
	90	5.9839		26.78	27.79	27.21
	89	6.0125		27.17	27.80	26.87
	86	5.9973		26.96	28.12	27.51
$P6_3/mmc$ -EuH ₉ ($Z = 2$)	130	3.5911 (3.5887)	5.5094 (5.5027)	30.76 (30.68)	30.01	29.34
	125	3.5870	5.5176	30.74	31.38	30.53
	121	3.5905	5.5265	30.85	31.67	30.85
	118	3.5992	5.5419	(31.085)	31.89	31.00
	116	3.5914	5.6063	31.31	32.07	31.19
	111	3.6203	5.5171	31.31	32.51	31.62
$F\bar{4}3m$ -EuH ₉ ($Z = 4$)	130	4.9475		30.27	30.67	29.92
	125	4.9472		30.27	30.98	30.28
	121	4.9566		30.44	31.26	30.57
	116	4.9741		30.77	31.63	30.90
	111	4.9786		30.85	32.04	31.33
	106	5.0313		31.84	32.43	31.67
	102	5.0439		32.08	32.76	32.00
	99	5.0589		32.37	33.01	32.23
	97	5.0700		32.58	33.20	32.42
	94	5.0765		32.71	33.48	32.71
	90	5.0866		32.90	33.82	32.93
	86	5.1088		33.33	34.15	33.39

Table S4. Calculated EoS parameters in the 3rd order Birch–Murnaghan equation with K_0' fixed 4 for $Pm\bar{3}n$ -Eu₈H₄₆, $P6_3/mmc$ -EuH₉, and $F\bar{4}3m$ -EuH₉. V_0 for all europium hydrides corresponds to 100 GPa.

	$Pm\bar{3}n$ -Eu ₈ H ₄₆	$P6_3/mmc$ -EuH ₉	$F\bar{4}3m$ -EuH ₉
V_0 (Å ³)	26.3(1)	31.9(1)	31.3(1)
K_0 (GPa)	471 ± 70	594 ± 70	699 ± 27
K_0'	4	4	4

Table S5. Relative energies (in kcal/mol) of the Eu clusters at different spin states.

Spin state (S_{total})	EuH ₂₈ ¹⁹⁺	EuH ₂₇ ¹⁸⁺	EuH ₂₄ ¹⁷⁺
0	207.78	235.09	211.30
1	91.34	100.62	112.89
2	80.32	84.52	84.40
3	0	9.73	64.18
4	9.62	0	0

Table S6. Occupancies of valence superatomic orbitals.

MO Type	Hexagonal EuH ₉		MO Type	Cubic EuH ₉		MO type	$Pm\bar{3}n$ -Eu ₈ H ₄₆	
	Alpha (↑)	Beta (↓)		Alpha (↑)	Beta (↓)		Alpha (↑)	Beta (↓)
F	0.97	-	F	0.97	-	F	0.98	-
F	0.97	-	F	0.97	-	F	0.98	-
F	0.97	-	F	0.97	-	F	0.98	-
F	0.97	-	F	0.97	-	F	0.98	-
F	0.97	-	F	0.96	-	F	0.97	-
F	0.97	-	F	0.96	-	F	0.96	-
F	0.96	-	F	0.96	-	F	0.96	-
D	0.95	0.77	D	0.79	0.78	D	0.59	0.58
D	0.78	0.76	D	0.79	0.77	D	0.59	0.58
D	0.77	0.74	P	0.68	0.70	D	0.59	0.56
D	0.74	0.72	P	0.68	0.70	D	0.56	0.55
D	0.72	0.67	P	0.68	0.70	D	0.55	0.54
P	-	0.65	S	-	0.65	P	-	0.54

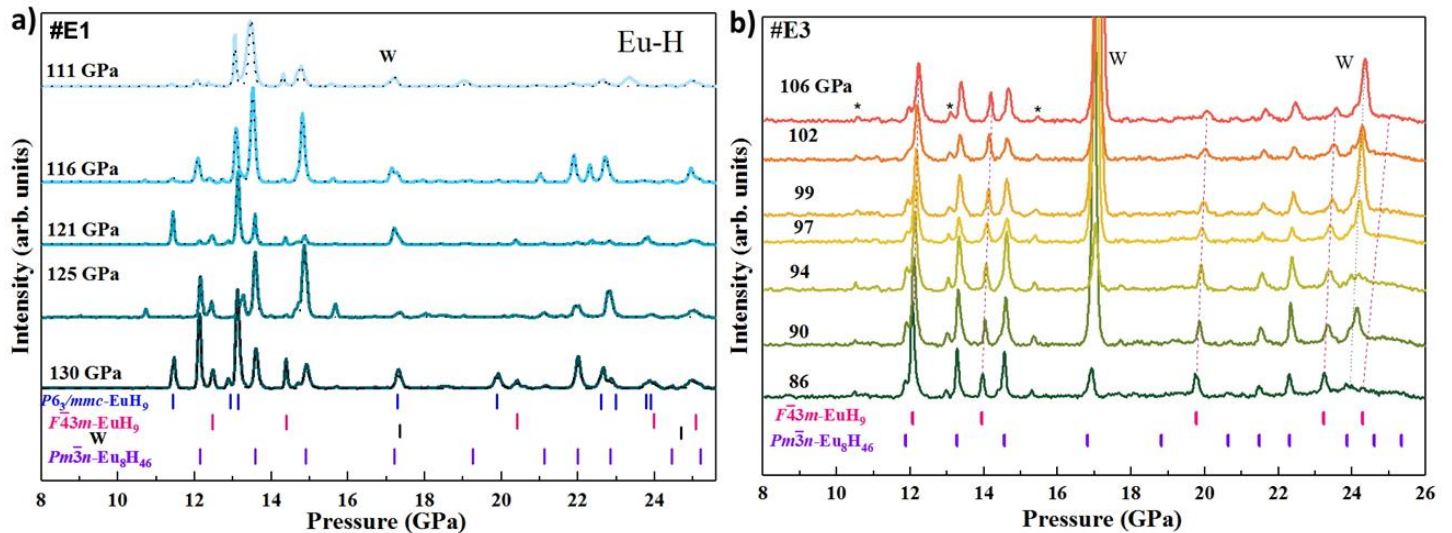


Figure S2. Decomposition of Eu polyhydrides after decreasing pressure in cell (a) #E1 and (b) #E3. The XRD patterns were indexed by $Pm\bar{3}n$ -Eu₈H₄₆, $P6_3/mmc$ -EuH₉, and $F\bar{4}3m$ -EuH₉. Dash lines are the model fit for the structures in Figures S2a.

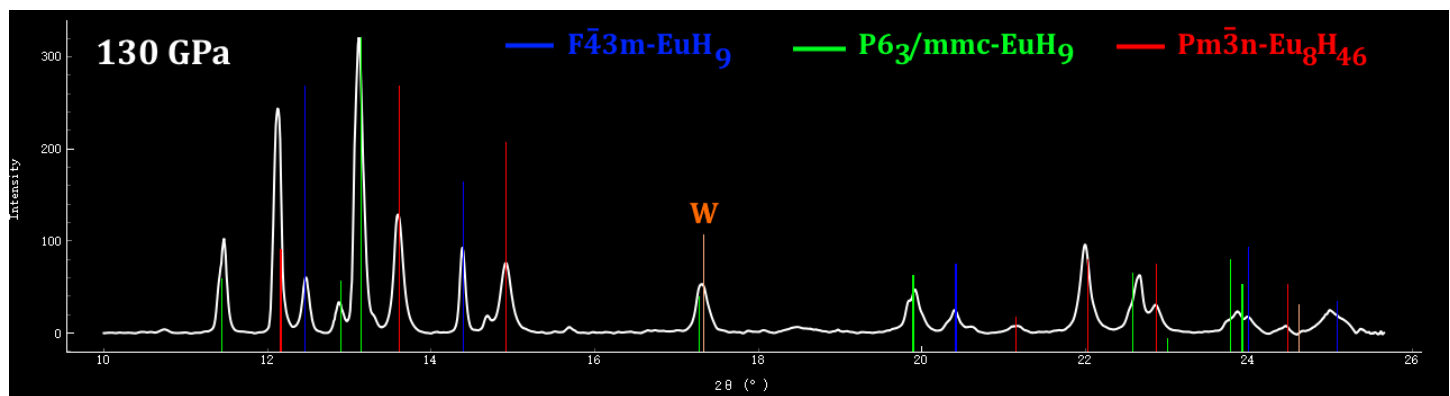


Figure S3. Qualitative correlation of the experimental reflections and simulated diffraction patterns of the Eu-H phases at 130 GPa, integrated using Dioptas software.

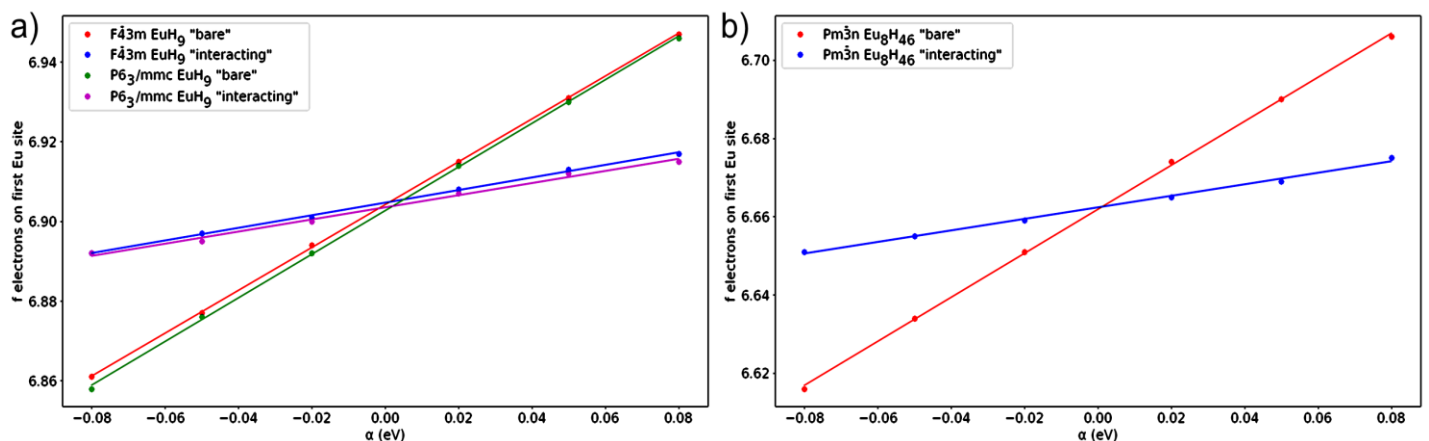


Figure S4. Linear response functions for (a) both EuH₉ phases and (b) the Eu₈H₄₆ phase. The calculated values are shown by dots; straight lines represent the least squares fit.

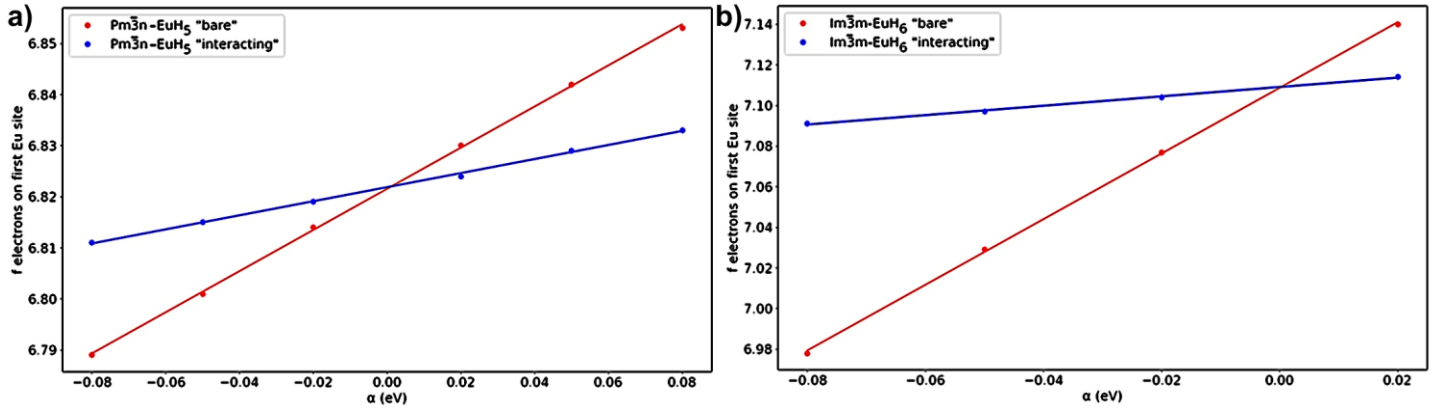


Figure S5. Linear response functions for (a) EuH₅ and (b) EuH₆ phases. The calculated values are shown by dots; straight lines represent the least squares fit.

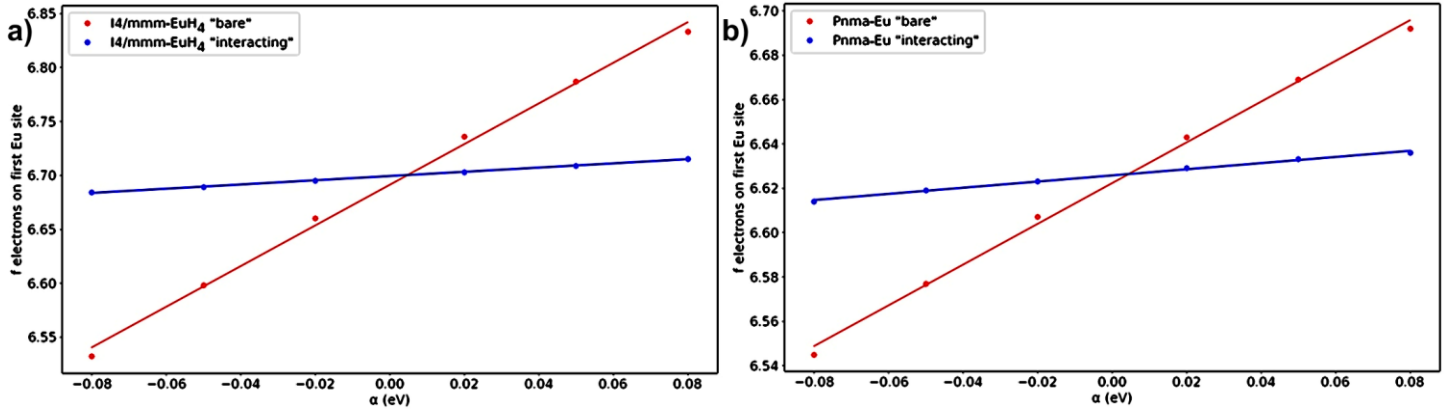


Figure S6. Linear response functions for (a) tetragonal EuH₄ and (b) pure Eu at 75 GPa. The calculated values are shown by dots; straight lines represent the least squares fit.

Table S7. Linear response functions and calculated U for the Eu–H phases at 130 GPa.

Phase	“Bare” response (eV ⁻¹)	“Interacting” response (eV ⁻¹)	$U-J$ (eV)
$F\bar{4}3m$ -EuH ₉	0.158	0.537	4.46
$P6_3/mmc$ -EuH ₉	0.152	0.547	4.74
$Pm\bar{3}n$ -Eu ₈ H ₄₆	0.147	0.562	5.01
$Im\bar{3}m$ -EuH ₆ *	0.231	1.616	3.7
$Pm\bar{3}n$ -EuH ₅	0.138	0.403	4.8
$I4/mmm$ -EuH ₄	0.196	1.884	4.6
$Pnma$ -Eu (75 GPa)	0.139	0.918	6.1

*For EuH₆, only perturbations up to 0.02 eV were included, because larger perturbations showed high nonlinearity.

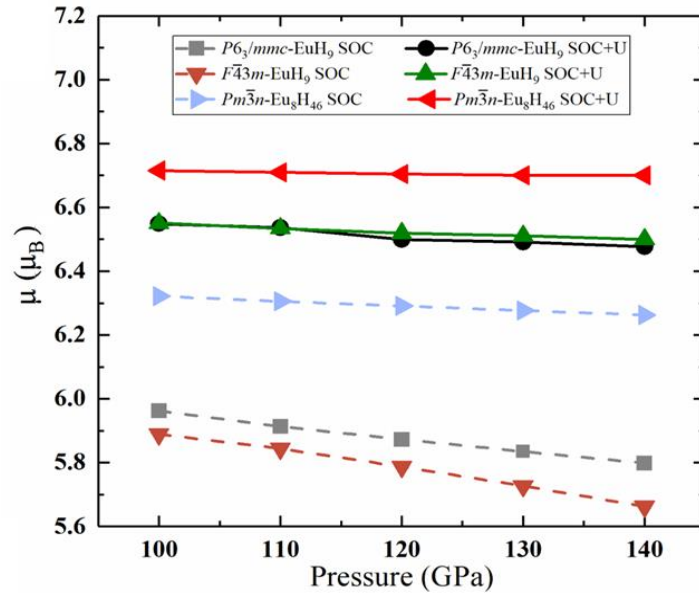


Figure S7. Magnetic moments (μ_B per 1 Eu atom) of all synthesized Eu-H compounds with and without U - J and SOC.

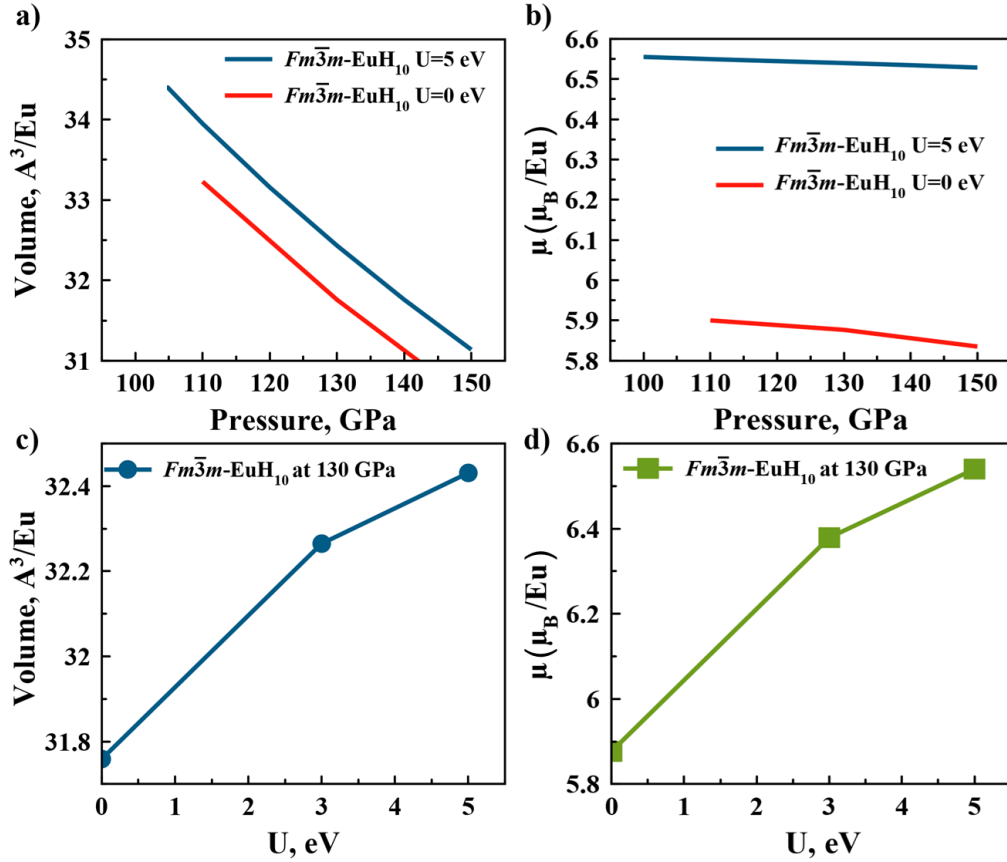


Figure S8. (a) Equation of state, (b) magnetic moment per 1 Eu atom, (c) dependence of the unit cell volume V on the Hubbard-like correction term U - J at 130 GPa, and (d) dependence of the magnetic moment on U - J at 130 GPa for the proposed $Fm\bar{3}m$ -EuH₁₀, isostructural to $Fm\bar{3}m$ -LaH₁₀.³⁸

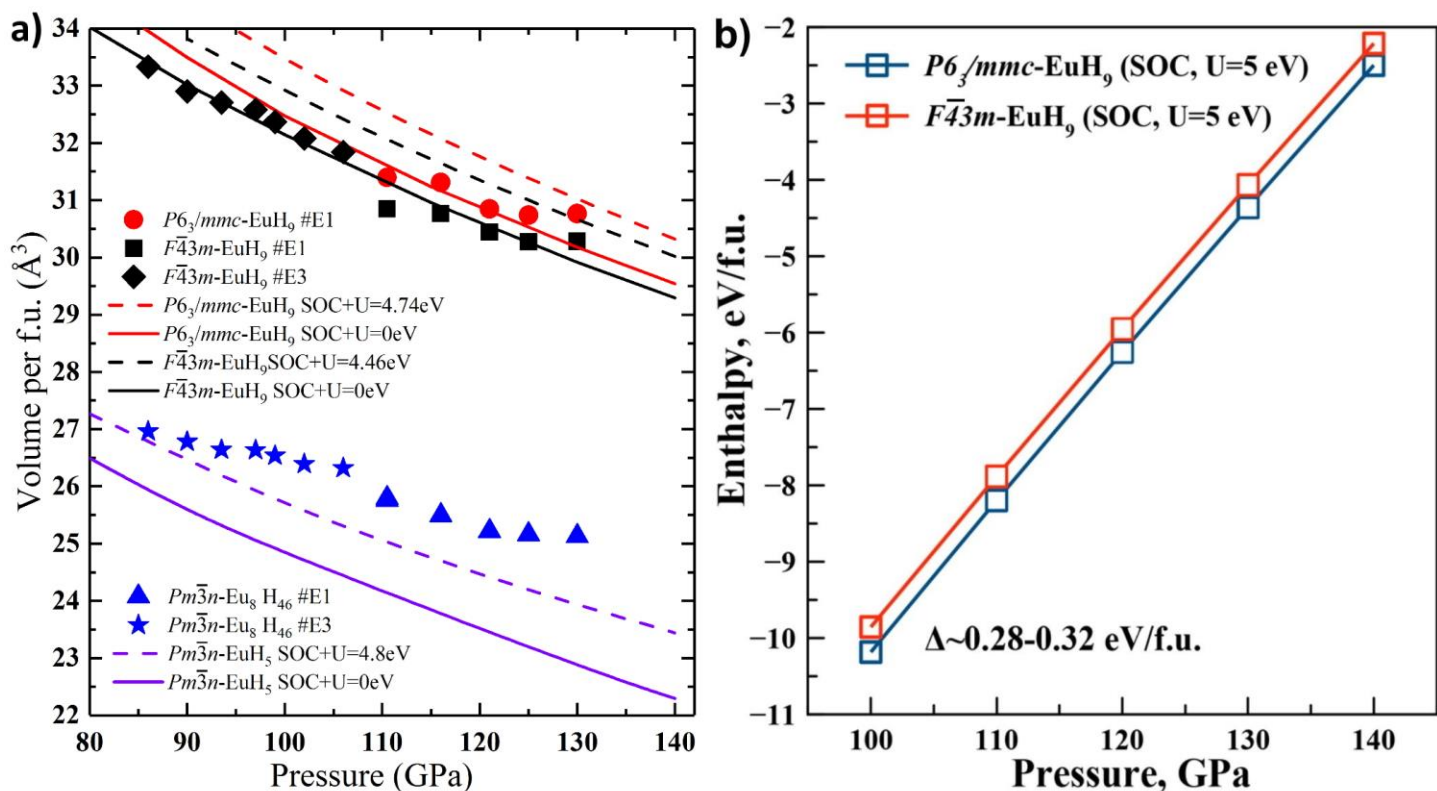


Figure S9. (a) Experimental cell volumes of the discovered Eu hydrides and calculated equations of states for $F\bar{4}3m$ -EuH₉, $P6_3/mmc$ -EuH₉, and proposed $Pm\bar{3}n$ -Eu₈H₄₆¹⁹ with SOC and U - J . (b) Difference between enthalpies of cubic and hexagonal modifications of EuH₉.

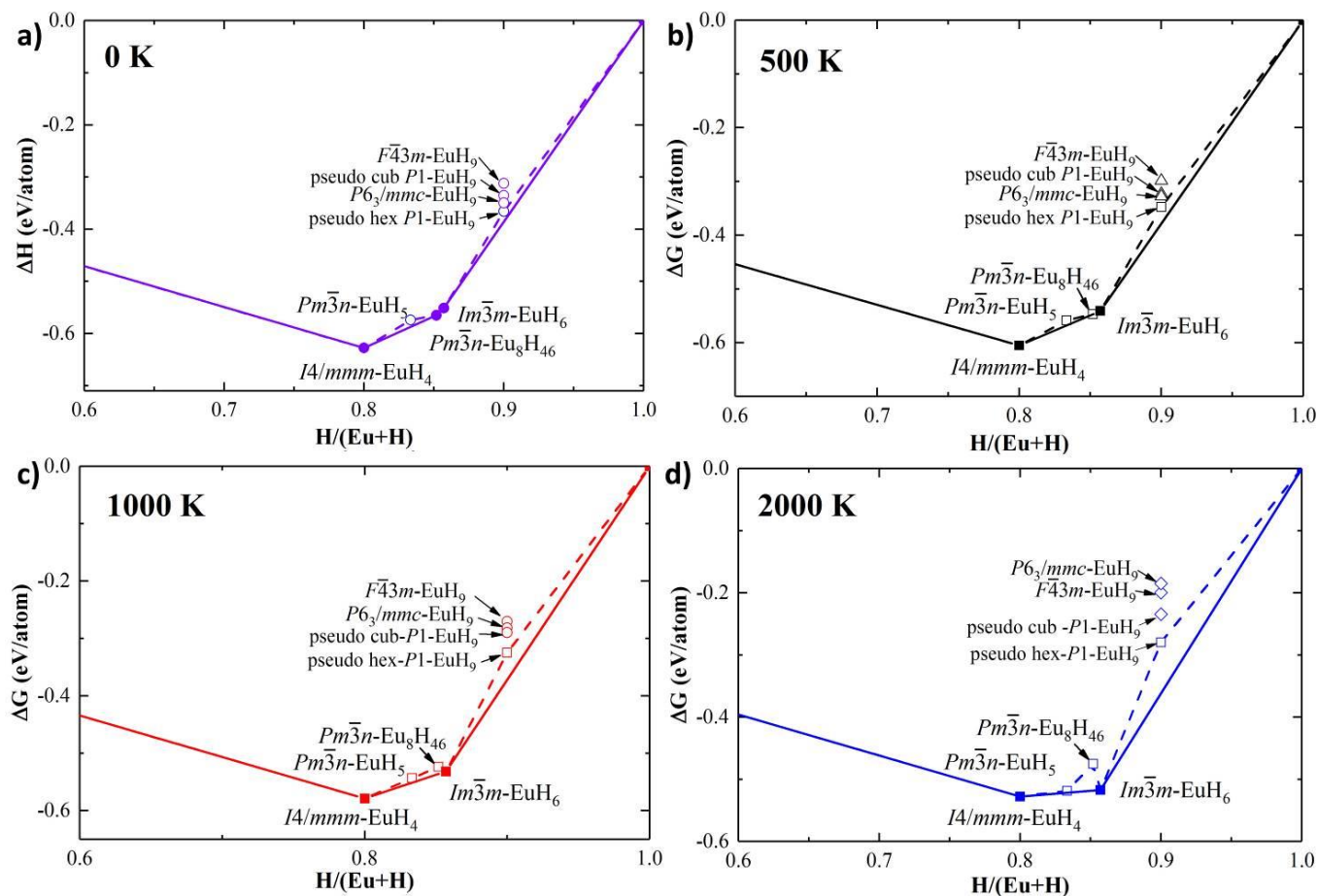


Figure S10. Calculated convex hulls of the Eu–H system at 130 GPa and (a) 0 K, (b) 500 K, (c) 1000 K, and (d) 2000 K with the the zero-point energy (ZPE), SOC, and $U-J$, specific for each compound (see Table S8).

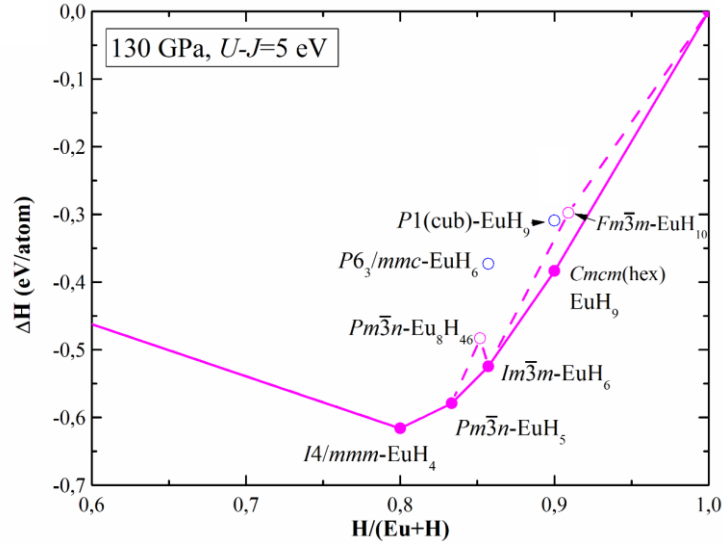


Figure S11. Calculated convex hulls of the Eu–H system at 130 GPa for 0 K with the ZPE, SOC, and fixed $U-J = 5$ eV.

Table S8. Enthalpy and energy of formation with and without the ZPE for various Eu–H phases at 130 GPa with SOC and $U-J$ (from Table S7).

Phase	Eu	H	x (H/Eu+H)	ZPE, eV/Eu	E+ZPE, eV/Eu	H_{form} , eV/Eu
<i>Pnma</i> -Eu	4	0	0	0.0047	5.42868	0
<i>I4/mmm</i> -EuH ₄	2	8	0.8	0.15492	−0.86015	−0.62783
<i>Pm</i> $\bar{3}$ <i>n</i> -EuH ₅	8	40	0.83333	0.19861	−0.85113	−0.57414
<i>Pm</i> $\bar{3}$ <i>n</i> -Eu ₈ H ₄₆	8	46	0.85185	0.20604	−1.94194	−0.56507
<i>Im</i> $\bar{3}$ <i>m</i> -EuH ₆	2	12	0.85714	0.21108	−2.90023	−0.5512
<i>F</i> $\bar{4}$ 3 <i>m</i> -EuH ₉	4	36	0.9	0.1459	−3.14065	−0.31209
<i>P</i> 6 ₃ / <i>mmc</i> -EuH ₉	2	18	0.9	0.19861	−4.75865	−0.34938
pseudocubic EuH ₉	2	1	0.9	0.34406	−5.13153	−0.33561
pseudohexagonal EuH ₉	4	1	0.9	0.35587	−4.99386	−0.36576
<i>C</i> 2/ <i>c</i> -H	0	24	1	0.00174	−0.78516	0

Table S9. Temperature dependence of the Gibbs free energy of formation (G_{form} , eV/atom), computed with the ZPE, SOC, and $U-J$ (from Table S7) for various Eu–H phases at 130 GPa.

Phase \ Temperature, K	0	500	1000	2000
<i>Pnma</i> -Eu	0	0	0	0
<i>I4/mmm</i> -EuH ₄	−0.62783	−0.60517	−0.57896	−0.52767
<i>Pm</i> $\bar{3}$ <i>n</i> -EuH ₅	−0.57414	−0.55873	−0.54337	−0.51834
<i>Pm</i> $\bar{3}$ <i>n</i> -Eu ₈ H ₄₆	−0.56507	−0.54654	−0.5233	−0.47524
<i>Im</i> $\bar{3}$ <i>m</i> -EuH ₆	−0.5512	−0.54096	−0.53178	−0.51735
<i>F</i> $\bar{4}$ 3 <i>m</i> -EuH ₉	−0.31209	−0.29836	−0.2704	−0.19966
<i>P</i> 6 ₃ / <i>mmc</i> -EuH ₉	−0.34938	−0.32308	−0.28185	−0.18473
pseudocubic EuH ₉	−0.33561	−0.31639	−0.28987	−0.23441
pseudohexagonal EuH ₉	−0.36576	−0.34746	−0.32449	−0.2797

C2/c-H	0	0	0	0
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Table S10. Results of the fixed-composition USPEX search for the best crystal structure of $Pm\bar{3}n$ -Eu₈H₄₆ at 130 GPa.

ID	Origin	Enthalpy	Volume (Å ³)	Density (g/cm ³)	Fitness (eV)
242	Permutate	-32.495	189.161	11.079	-32.495
159	keptBest	-32.494	189.161	11.079	-32.494
70	keptBest	-32.488	189.161	11.079	-32.488
37	Seeds	-32.485	189.161	11.079	-32.485
114	keptBest	-28.975	189.161	11.079	-28.975
197	keptBest	-28.474	189.161	11.079	-28.474
247	Permutate	-27.51	186.344	11.247	-27.51
127	keptBest	-27.458	185.838	11.277	-27.458
8	Random	-22.699	180.853	11.588	-22.699
271	softmutate	-22.578	181.419	11.552	-22.578
295	softmutate	-22.225	186.344	11.247	-22.225
272	softmutate	-22.049	181.419	11.552	-22.049
42	RandTop	-21.987	180.853	11.588	-21.987
200	Heredity	-21.948	184.714	11.346	-21.948
199	Heredity	-21.858	185.893	11.274	-21.858
131	softmutate	-21.418	186.344	11.247	-21.418
232	keptBest	-20.476	181.412	11.552	-20.476
324	Heredity	-20.359	185.809	11.279	-20.359
79	Heredity	-20.276	185.837	11.277	-20.276
78	softmutate	-20.162	180.825	11.59	-20.162
196	Random	-19.428	181.706	11.534	-19.428
73	keptBest	-19.278	180.853	11.588	-19.278
123	Permutate	-18.845	189.161	11.079	-18.845
284	Heredity	-18.6	188.341	11.127	-18.6
246	keptBest	-18.43	180.853	11.588	-18.43
283	Random	-18.119	182.093	11.509	-18.119

Additional Le Bail Refinements

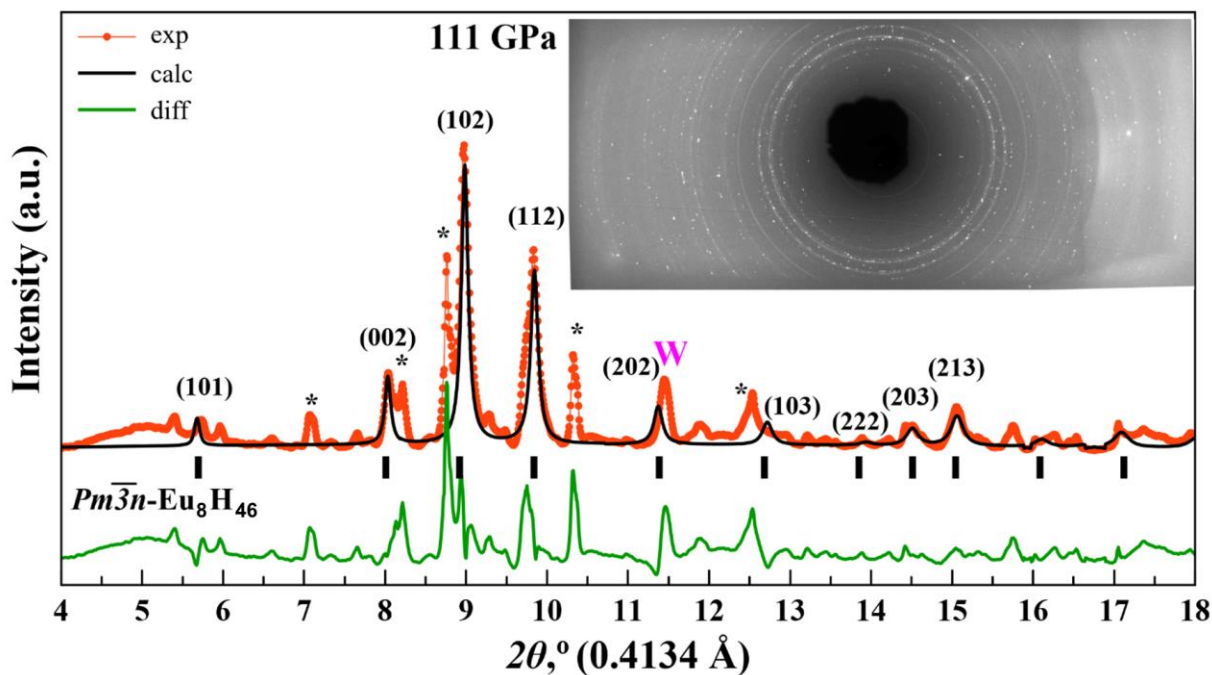


Figure S12. Experimental XRD pattern (cell #E1) and the Le Bail refinement of the main phase — $Pm\bar{3}n$ -Eu₈H₄₆ at 111 GPa. Unexplained peaks are marked by asterisks.

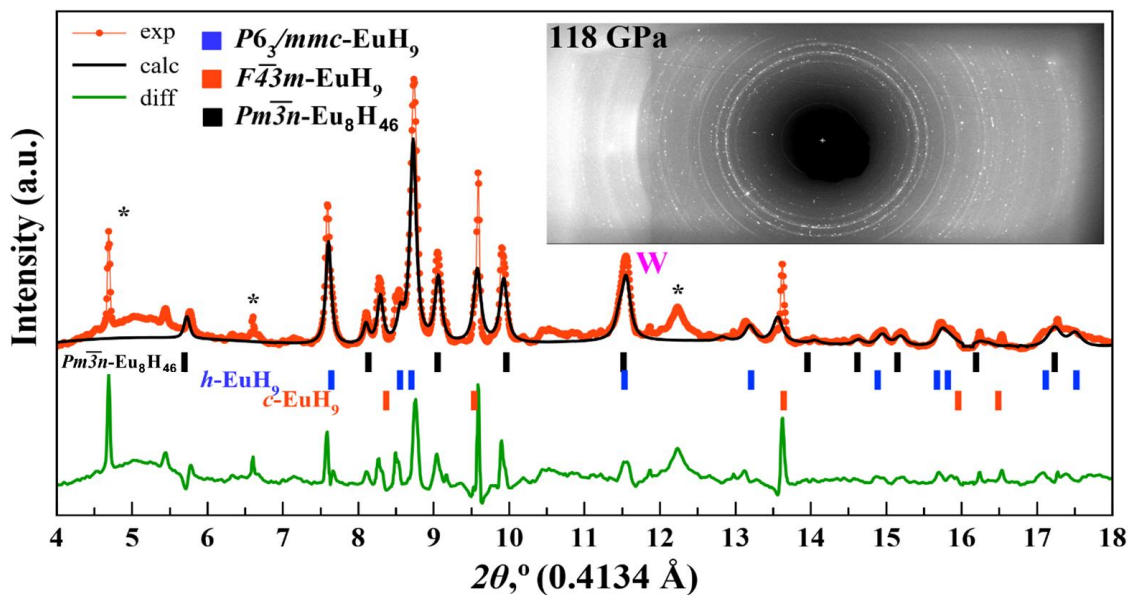


Figure S13. Experimental XRD pattern (cell #E1) and the Le Bail refinement of $F\bar{4}3m$ -EuH₉, $P6_3/mmc$ -EuH₉, and $Pm\bar{3}n$ -Eu₈H₄₆ at 118 GPa. Unexplained peaks are marked by asterisks.

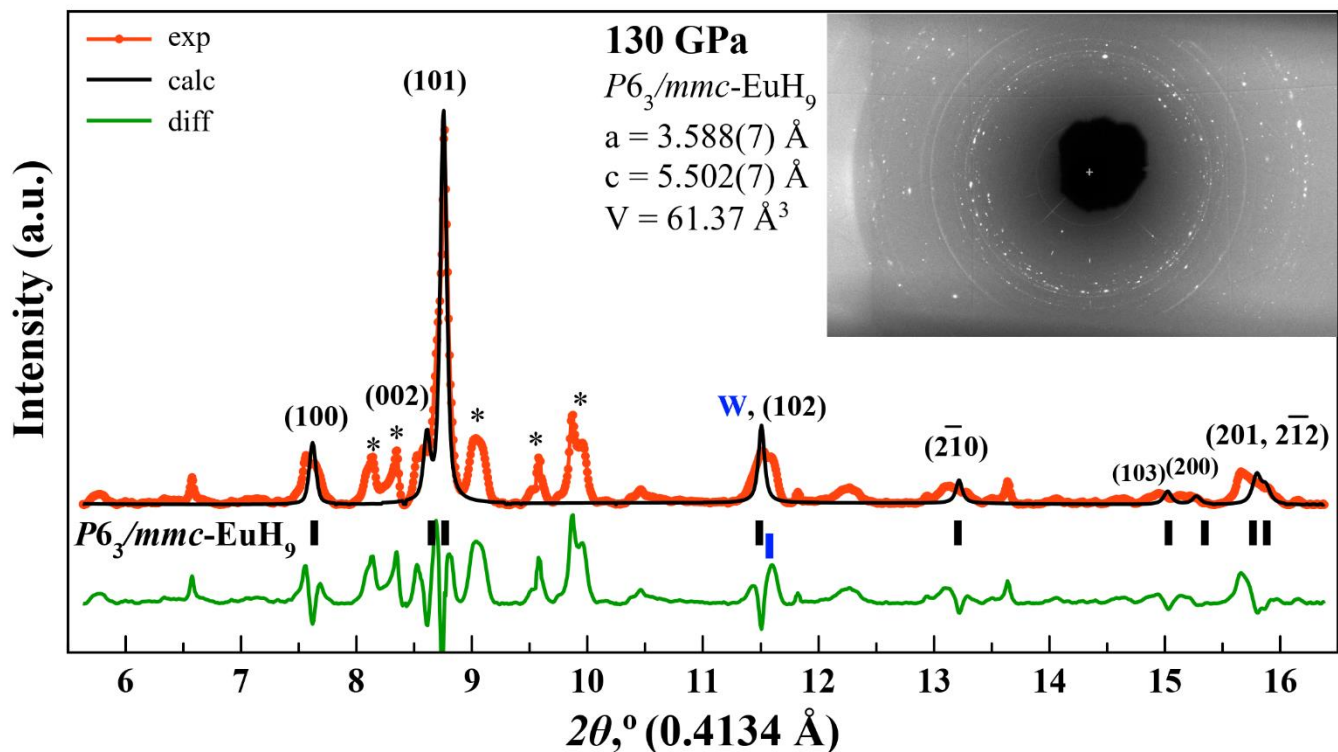


Figure S14. Experimental XRD pattern (cell #E1) and the Le Bail refinement of the main phase — $P6_3/mmc$ -EuH₉ at 130 GPa. Unexplained peaks are marked by asterisks.

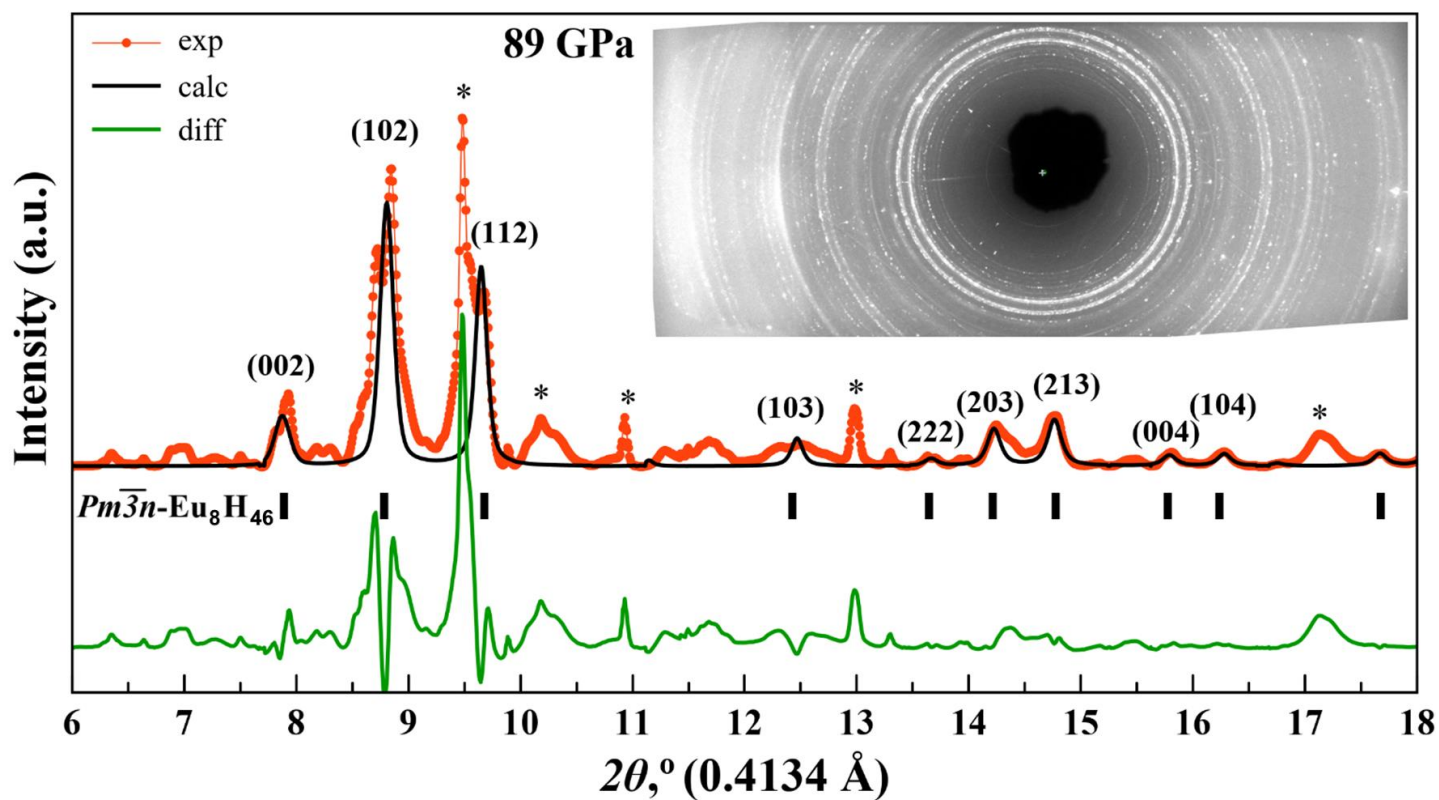


Figure S15. Experimental XRD pattern (cell #E2) and the Le Bail refinement of the main phase — $Pm\bar{3}n$ -Eu₈H₄₆ at 89 GPa. Unexplained peaks are marked by asterisks.

Magnetic Structure

The first step in a detailed study of the magnetic configurations of all europium hydrides is to determine which collinear magnetic ordering is preferable: ferromagnetic (FM) or antiferromagnetic (AFM). If we neglect the spin–orbit coupling, then only the magnitude of magnetic moments is meaningful and we should consider only one possible FM configuration, where the magnetic moments of the Eu atoms point in the same direction. The number of possible AFM configurations, instead, is in principle infinite, since it is always possible to find a new configuration, with half of the spins pointing up and the other half pointing down, by enlarging the unit cell. For this reason, we studied all possible AFM configurations only up to the Eu_4H_{36} supercell for the EuH_9 stoichiometry. We generated our trial configurations using the derivative structure enumeration library *enumlib*,³⁹ in which the minimum size able to represent an AFM configuration is always chosen as the size of the unit cell. In other words, if we consider Eu atoms with different spin states as different atomic types, we turn out to always work with primitive cells. We obtained a total of seven AFM configurations for $F\bar{4}3m\text{-EuH}_9$ and five configurations for $P6_3/mmc\text{-EuH}_9$, as shown in Figure 4g,h.

Then we performed a full relaxation of both EuH_9 phases at 130 GPa without SOC for our eight (seven AFM and one FM) or six (five AFM and one FM) magnetic configurations. All of them successfully completed the process, but after relaxation some of the AFM configurations displayed distorted geometries, with symmetry and enthalpy lower than those of the ideal cubic or hexagonal phase (Table S9).

To explore the magnetic properties of $Pm\bar{3}n\text{-Eu}_8\text{H}_{46}$, we examined 15 trial configurations: one FM and 14 AFM (Figure S16). All of them completed relaxation without a change in the orientation of the magnetic moments. As in the case of EuH_9 , some of the AFM configurations displayed a distorted geometry after relaxation (Table S11). We investigated the space group of all relaxed structures with increasing tolerances and found all distortions becoming negligible if a tolerance of 0.2 is used.

Magnetic anisotropy has been investigated by performing single-point energy calculations with SOC on a FM and an AFM configuration for each of our phases (ideal and distorted ones), with the magnetic moments aligned along seven different directions (Table S12). We expect a little magnetic anisotropy for all phases with EuH_9 stoichiometry, for which we identified the most stable orientation of the magnetic moments. For $Pm\bar{3}n\text{-Eu}_8\text{H}_{46}$ we do not expect any magnetic anisotropy since different orientations of the magnetic moments have almost the same enthalpy up to numerical errors.

Table S11. Enthalpy and space groups of the trial magnetic structures after full relaxation without SOC at 130 GPa. The space groups were determined with a tolerance of 0.1.

	Configuration	Enthalpy (meV/Eu atom)	Space group
$F\bar{4}3m$ -EuH ₉	FM	470.32	$F\bar{4}3m$
	AFM1	0.0	$P1$
	AFM2	440.52	$F\bar{4}3m$
	AFM3	154.85	$Imm2$
	AFM4	165.9	$Imm2$
	AFM5	167.95	$Imm2$
	AFM6	447.47	$F\bar{4}3m$
	AFM7	180.47	$Imm2$
$P6_3/mmc$ -EuH ₉	FM	197.37	$P6_3/mmc$
	AFM1	215.26	$P6_3/mmc$
	AFM2	213.95	$P6_3/mmc$
	AFM3	0.0	$Cmcm$
	AFM4	59.26	$C2$
	AFM5	8.2	$Cmcm$
$Pm\bar{3}n$ -Eu ₈ H ₄₆	FM	0.0	$Pm\bar{3}n$
	AFM1	56.92	$Pm\bar{3}n$
	AFM2	64.78	$Pm\bar{3}n$
	AFM3	64.73	$Pm\bar{3}n$
	AFM4	56.39	$Pm\bar{3}n$
	AFM5	56.68	$P4_2/mmc$
	AFM6	66.69	$Pm\bar{3}n$
	AFM7	66.66	$Pm\bar{3}n$
	AFM8	56.11	$P4_2/mmc$
	AFM9	56.39	$Pm\bar{3}n$
	AFM10	66.59	$Pm\bar{3}n$
	AFM11	66.63	$Pm\bar{3}n$
	AFM12	56.92	$Pm\bar{3}n$
	AFM13	64.74	$Pm\bar{3}n$
	AFM14	64.75	$Pm\bar{3}n$

Table S12. Single-point enthalpies of FM and AFM configurations for both EuH₉ and $Pm\bar{3}n$ -Eu₈H₄₆ (including the distorted structures *P1*, *Imm2*, *Cmcm*, *C2*), calculated with SOC and with the magnetic moments aligned along seven different directions at 130 GPa.

Configuration	Enthalpy (meV/atom)						
<i>P1</i> (cub)-EuH ₉	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>XY</i>	<i>XZ</i>	<i>YZ</i>	<i>XYZ</i>
FM	-	1.047*	-	-	0.000*	0.532*	0.791*
AFM1	-	0.617	-	0.158*	-	0.430	0.115
<i>Imm2</i> (cub)-EuH ₉							
FM	26.928	26.651	27.085	26.78	26.994	26.277	26.471
AFM3	0.871	0.833	1.392	0.849	1.131	0.0	0.291
<i>F43m</i> -EuH ₉							
FM	30.226	30.283	30.275	30.272	30.244	30.318	30.281
AFM2	0.0	0.41	0.205	0.171	0.076	0.652	0.397
<i>Cmcm</i> (hex)-EuH ₉							
FM	7.691	8.878	7.309	8.289	7.489	8.12	7.958
AFM3	0.076	1.4	0.0	0.722	0.01	0.827	0.548
<i>C2</i> (hex)-EuH ₉							
FM	0.563	0.0	0.396	0.296	0.767	0.185	0.498
AFM4	6.517	5.65	6.018	6.091	6.386	5.816	6.12
<i>P6₃/mmc</i> -EuH ₉							
FM	0.176	0.176	0.0	0.174	0.118	0.128	0.152
AFM1	19.372	19.371	18.4	19.368	18.855	18.874	19.028
$Pm\bar{3}n$ -Eu ₈ H ₄₆							
FM	0.057	0.057	0.057	0.023	0.022	0.016	0.0
AFM	57.988	58.035	58.035	58.009	58.009	58.021	57.999

“-” means the convergence was not reached after 200 electronic steps.

* Magnetic moments changed the orientation.

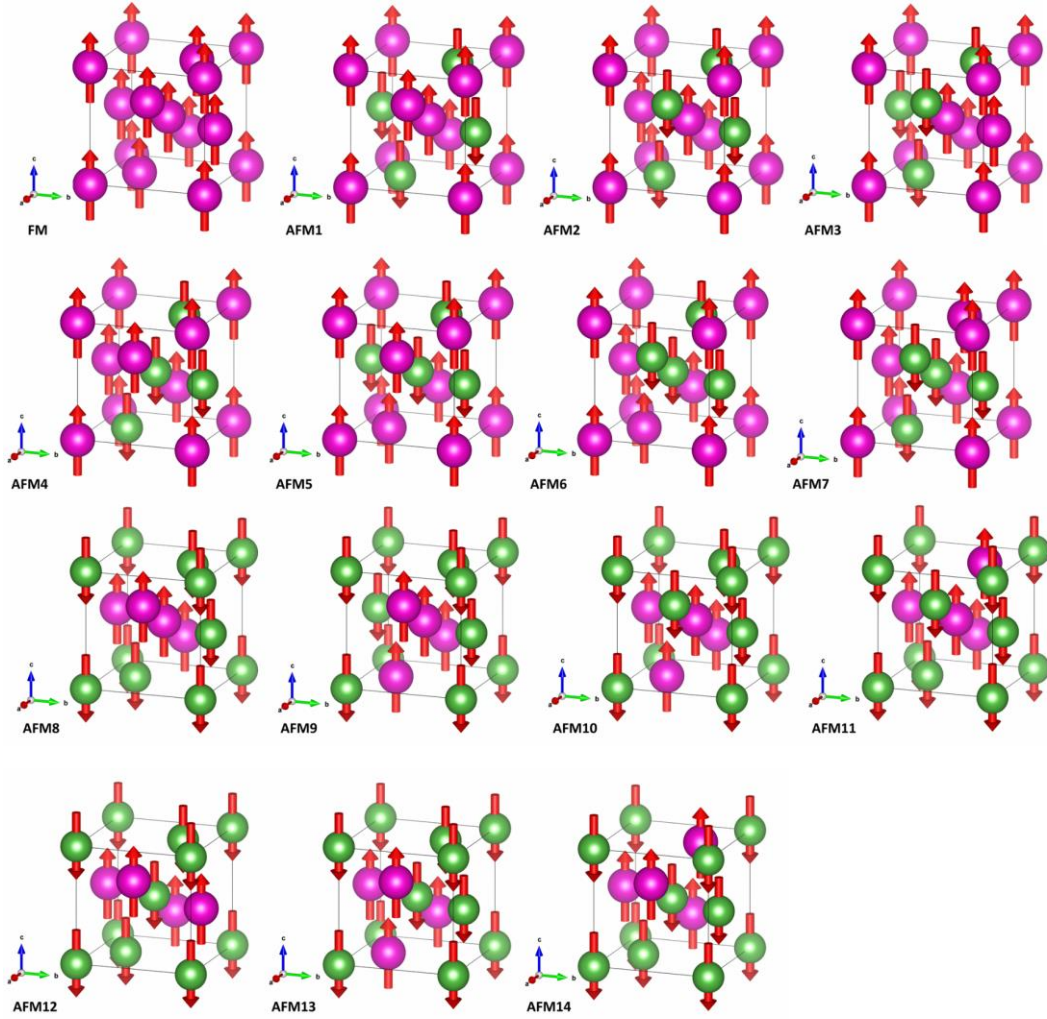


Figure S16. 15 trial magnetic configurations for $Pm\bar{3}n$ -Eu₈H₄₆ used in this work.

To study the Néel temperature of $F\bar{4}3m$ -EuH₉ and the Curie temperature of $P6_3/mmc$ -EuH₉, we relaxed two additional independent AFM configurations for each geometry with SOC and the magnetic moments aligned along the x axis and z axis, respectively. We used magnetic moments aligned along the z axis to study the Curie temperature of ferromagnetic $Pm\bar{3}n$ -Eu₈H₄₆. The final enthalpies and magnetic moment orientations are shown in Table S13, whereas the absolute value of the magnetic moment on each Eu atom after relaxation was always close to $6.8 \mu_B$ for EuH₉ and $6.9 \mu_B$ for Eu₈H₄₆.

Taking into account the crystal periodicity, in the unit cell of $F\bar{4}3m$ -EuH₉ we found 24 links between the Eu atoms at 3.51 \AA and 12 links at 4.96 \AA at 130 GPa. In the unit cell of $P6_3/mmc$ -EuH₉, we found 12 links at 3.49 \AA and 12 links at 3.55 \AA . Then we modeled the magnetic interaction with the Ising Hamiltonian:

$$H = H_0 - \frac{1}{2}J_1 \sum_{i \neq j} S_i \cdot S_j - \frac{1}{2}J_2 \sum_{i \neq j} S_i \cdot S_j \quad (\text{S1})$$

where J_1 and J_2 are the coupling constants assigned to the two groups of neighbors, H_0 is a constant term which does not depend on the magnetic interaction, and S_i is $+1$ or -1 , depending on the spin orientation of the respective Eu atom. This Hamiltonian for EuH₉ takes into account the magnetic interactions only up to the second nearest neighbors.

Table S13. Magnetic moment orientations and calculated enthalpies of the three magnetic configurations used for studying the Néel temperature of EuH₉ and of the four magnetic configurations used for studying the Curie temperature of $Pm\bar{3}n$ -Eu₈H₄₆. +/- mark the direction of magnetic moments along the *z* axis.

<i>F</i> $\bar{4}3m$ -EuH ₉									
	Eu1		Eu2		Eu3		Eu4		Enthalpy (meV/Eu atom)
FM	+		+		+		+		31.2
AFM2	+		+		−		−		0.0
AFM5	+		−		+		−		8.3
<i>P</i> 6 ₃ / <i>mmc</i> -EuH ₉									
	Eu1		Eu2		Eu3		Eu4		Enthalpy (meV/Eu atom)
FM	+		+		+		+		0.0
AFM1	+		−		+		−		20.0
AFM3	+		+		−		−		16.7
<i>Pm</i> $\bar{3}n$ -Eu ₈ H ₄₆									
	Eu1	Eu2	Eu3	Eu4	Eu5	Eu6	Eu7	Eu8	Enthalpy (meV/Eu atom)
FM	+	+	+	+	+	+	+	+	0.0
AFM1	+	+	+	+	−	−	−	−	58.0
AFM5	+	−	+	+	−	−	−	+	57.0
AFM8	+	−	+	−	+	−	+	−	66.9

In the primitive cell of Eu₈H₄₆, we found six links between the Eu atoms at 2.95 Å, 24 links at 3.29 Å, and 24 links at 3.61 Å. We modeled the magnetic interaction with the Ising Hamiltonian:

$$H = H_0 - \frac{1}{2}J_1 \sum_{i \neq j} S_i \cdot S_j - \frac{1}{2}J_2 \sum_{i \neq j} S_i \cdot S_j - \frac{1}{2}J_3 \sum_{i \neq j} S_i \cdot S_j \quad (S2)$$

where J_1 , J_2 , and J_3 are the coupling constants assigned to the three groups of neighbors mentioned above. This Ising Hamiltonian takes into account the magnetic interactions up to the 3rd nearest neighbors for Eu₈H₄₆.

The values of the coupling constants of each phase can be obtained from the enthalpies of our three magnetic configurations by solving the system of equations for H_0 , J_1 , J_2 , and J_3 . The critical temperatures in our Heisenberg model were obtained from a Monte Carlo simulation as implemented in the VAMPIRE code.⁴⁰ The size of the simulation box was 8×8×8 nm for EuH₉ and 10×10×10 nm for Eu₈H₄₆ after the convergence tests, and the transition temperature was found as the value where the normalized mean magnetization length goes below 0.25. The obtained values of the coupling constants and the Néel or Curie temperatures are listed in Tables S14-16, the mean magnetization length is plotted vs. temperature in Figure S17. Obtained normalized $\mu(T)$ dependencies may be approximated well by the Curie–Weiss type formula $a+b \cdot (T_{C,N} - T)^{1/2}$, with $b = 0.115$ (*c*-EuH₉), 0.066 (*h*-EuH₉) and 0.042 (Eu₈H₄₆).

Table S14. Coupling constants (in Joules) and the estimated critical temperatures of both EuH₉ phases and $Pm\bar{3}n$ -Eu₈H₄₆.

	J_1 (J per Eu–Eu link)	J_2 (J per Eu–Eu link)	J_3 (J per Eu–Eu link)	$T_{C,N}$ (K)
<i>F</i> $\bar{4}3m$ -EuH ₉	−6.2578e−22	1.8056e−23	−	24
<i>P</i> 6 ₃ / <i>mmc</i> -EuH ₉	2.6834e−22	5.3336e−22	−	137
<i>Pm</i> $\bar{3}n$ -Eu ₈ H ₄₆	2.5042e−21	1.4070e−21	9.1531e−22	336

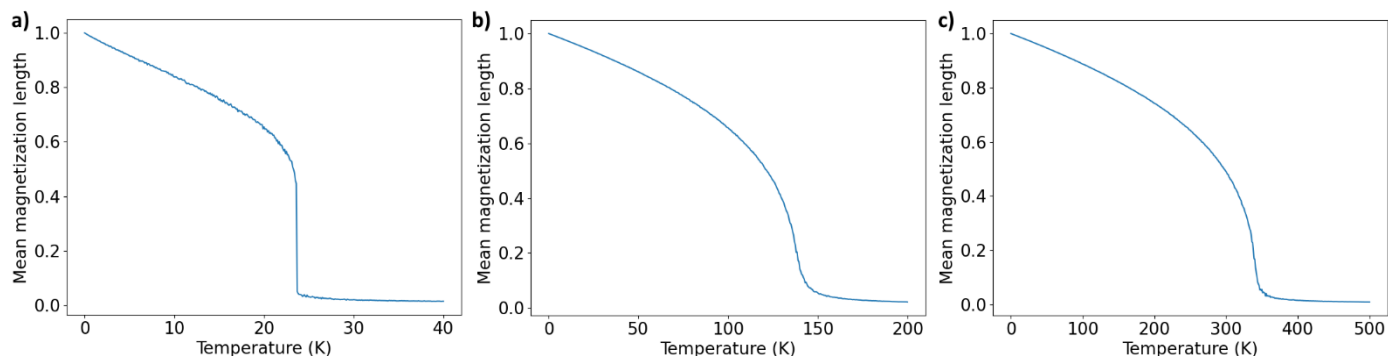


Figure S17. Normalized mean magnetization lengths with respect to temperature in (a) $F\bar{4}3m$ -EuH₉, (b) $P6_3/mmc$ -EuH₉, and (c) $Pm\bar{3}n$ -Eu₈H₄₆ from the Monte Carlo simulations. For antiferromagnetic $F\bar{4}3m$ -EuH₉ the mean magnetization length of the spin-up channel is displayed.

We chose to truncate the Ising Hamiltonian for the EuH₉ phases to 2nd nearest neighbor interactions on the basis of a convergence test. For $F\bar{4}3m$ -EuH₉, we first calculated J_1 from all combinations of enthalpies listed in Table S13, obtaining quite similar values (Table S15). The extension of our Ising Hamiltonian to the 2nd neighbor interactions was dictated only by the possibility of increasing the precision. For $P6_3/mmc$ -EuH₉, the values of J_1 for all possible combinations of calculated enthalpies are displayed in Table S15. In one case the system of equations was singular, and in the two remaining cases the calculated values of J_1 are very different. The negative value of J_1 is unphysical because it denotes an AFM ordering, but our system is ferromagnetic. Therefore, we chose to include the second neighbor interactions in our Ising Hamiltonian. We expected them to be of crucial importance in $P6_3/mmc$ -EuH₉ because they are equally abundant and their distance $d(\text{Eu-Eu})$ is only 0.06 Å larger compared with the first neighbor interactions. We did not include the 3rd neighbor interactions because their distance, 4.98 Å, is significantly higher than that of the first and the second neighbor interactions and they are equally abundant in the unit cell.

Table S15. Values of J_1 (in Joules) for both EuH₉ phases and Eu₈H₄₆, obtained from different combinations of magnetic configurations.

Phase	Combination	J_1 (J per Eu-Eu link)
$F\bar{4}3m$ -EuH ₉	FM, AFM2	$-6.2578\text{e-}22$
	FM, AFM5	$-6.1375\text{e-}22$
	AFM2, AFM5	$-6.6190\text{e-}22$
$P6_3/mmc$ -EuH ₉	FM, AFM2	singular
	FM, AFM5	$6.6836\text{e-}22$
	AFM2, AFM5	$-1.3168\text{e-}22$
$Pm\bar{3}n$ -Eu ₈ H ₄₆	FM, AFM1	singular
	FM, AFM5	$1.8269\text{e-}20$
	FM, AFM8	$7.1488\text{e-}21$
	AFM1, AFM5	$-3.0969\text{e-}22$
	AFM1, AFM8	$9.5606\text{e-}22$
	AFM5, AFM8	$1.5889\text{e-}21$

The choice to truncate the Ising Hamiltonian for Eu₈H₄₆ to the 3rd nearest neighbor interactions is also the result of a convergence test. In principle, we could have used only the nearest neighbors, calculating J_1 from any

combination of two enthalpies from Table S13 that gives a nonsingular system of equations. The resulting values of J_1 are presented in Table S15. The results are very dependent on the choice of the systems, and in one case we got a negative value of J_1 , which is unphysical because it denotes an AFM ordering, whereas our system is ferromagnetic. In a similar fashion, we could have truncated our Ising Hamiltonian at the 2nd nearest neighbors. In this case we need three relaxed magnetic configurations to calculate J_1 and J_2 . The results for all possible choices are listed in Table S16 together with the respective Curie temperatures from Monte Carlo simulations.

Table S16. Values of J_1 , J_2 (in Joules) and T_C for Eu_8H_{46} obtained from different combinations of magnetic configurations.

Phase	Combination	J_1 (J per Eu–Eu link)	J_2 (J per Eu–Eu link)	T_C (K)
$Pm\bar{3}n\text{-Eu}_8\text{H}_{46}$	FM, AFM1, AFM5	4.3349e–21	2.3323e–21	376
	FM, AFM1, AFM8	2.5042e–21	2.3223e–21	338
	FM, AFM5, AFM8	1.5889e–21	2.7799e–21	374
	AFM1, AFM5, AFM8	1.5889e–21	9.4931e–22	152

For the first three combinations, the obtained values of J_2 are very close to each other. The 2nd nearest neighbor interaction in $Pm\bar{3}n\text{-Eu}_8\text{H}_{46}$ turns out to be more important than the nearest neighbor interaction because the values of the coupling constants J_1 and J_2 are comparable and the number of second nearest neighbor interactions is four times higher. This is the main reason why the first three Curie temperatures are also close. The results in the last row of Table S14 are most probably due to numerical errors because the enthalpies of the three AFM configurations are relatively close to each other (Table S11). For our calculation of T_C for Eu_8H_{46} , we chose to take another step forward in accuracy by writing our Ising Hamiltonian up to the 3rd nearest neighbors.

A somewhat more complicated case is pseudo-hexagonal $Cmcm\text{-EuH}_9$ (Table S12). In order to study the Néel temperature of this phase we checked firstly how much the distances between neighbouring atoms changed with respect to the high-symmetry $P6_3/mmc$ modification. For computing the Curie temperature of FM $P6_3/mmc\text{-EuH}_9$, we wrote the Ising Hamiltonian up to the second nearest neighbors. The situation is different for $Cmcm\text{-EuH}_9$, where the first and the second neighbours' distances split into three groups. In the $Cmcm\text{-Eu}_4\text{H}_{36}$ supercell there are 8 Eu–Eu links at 3.47 Å, 8 links at a distance between 3.52 Å and 3.55 Å and 8 links at 3.61 Å. The next group of neighbours are located at more than 5 Å and therefore we did not take them into account. We figured out that this structural feature of the $Cmcm$ is responsible for the increased stability of the AFM3 (Figure 4h) magnetic state compared to the FM state of $P6_3/mmc$ modification.

In the $Cmcm\text{-Eu}_4\text{H}_{36}$ two more AFM configurations are possible other than AFM3. Together with the FM state, four magnetic configurations are enough to compute three coupling constants (J_1 , J_2 , J_3) only if they give rise to a non-singular system of equations. Unfortunately, this is not the case for $Cmcm$ phase, therefore the coupling constants were computed by using the FM state and three independent AFM configurations in the bigger supercell Eu_8H_{72} . As a result we found: $J_1 = 4.7416 \times 10^{-22}$ J, $J_2 = 1.1398 \times 10^{-21}$ J, $J_3 = -1.9388 \times 10^{-21}$ J.

Monte Carlo simulation on the AFM3 magnetic state in the unit cell $Cmcm\text{-Eu}_4\text{H}_{36}$ using found coupling constants indicates that the AFM3 magnetic ordering is stable only at 0 K, while it collapses at any finite temperature. Among all 76 possible AFM configurations in the supercell Eu_8H_{72} we found that one configuration, denoted here as AFM10, is more stable than the previously described AFM3. However, the Monte Carlo simulation on AFM10 gives the same result as for AFM3. Thus, we can conclude that $Cmcm\text{-EuH}_9$ does not exhibit magnetism at finite temperatures. This conclusion is very important from the point of view of a possible manifestation of superconductivity in pseudo-hexagonal EuH_9 .

Natural Population Analysis

Table S17. Occupancies ($|e|$) of localized bonding elements obtained via the SSAdNDP method.

	<i>P6₃/mmc</i> - CeH ₉ (100 GPa)	<i>F43m</i> - PrH ₉ (100 GPa)	<i>P6₃/mmc</i> - PrH ₉ (100 GPa)	<i>P6₃/mmc</i> - NdH ₉ (100 GPa)	<i>Fm3m</i> - LaH ₁₀ (150 GPa)	<i>Fm3m</i> - YH ₁₀ (400 GPa)
1c–2e (s-type lone pairs)	1.84	1.84	1.84	1.85	1.71	1.96
Three 1c–2e (p-type lone pairs)	1.94	1.95	1.95	1.95	1.89	1.98
Five <i>nc</i> –2e*	1.35–1.25	1.44–1.16	1.38–1.29	1.44–1.21	1.65–1.54	1.66–1.56
One <i>nc</i> –2e*	1.17	1.08	1.23	1.19	1.48	1.51

* *n* is the number of the hydrogen atoms in the cage.

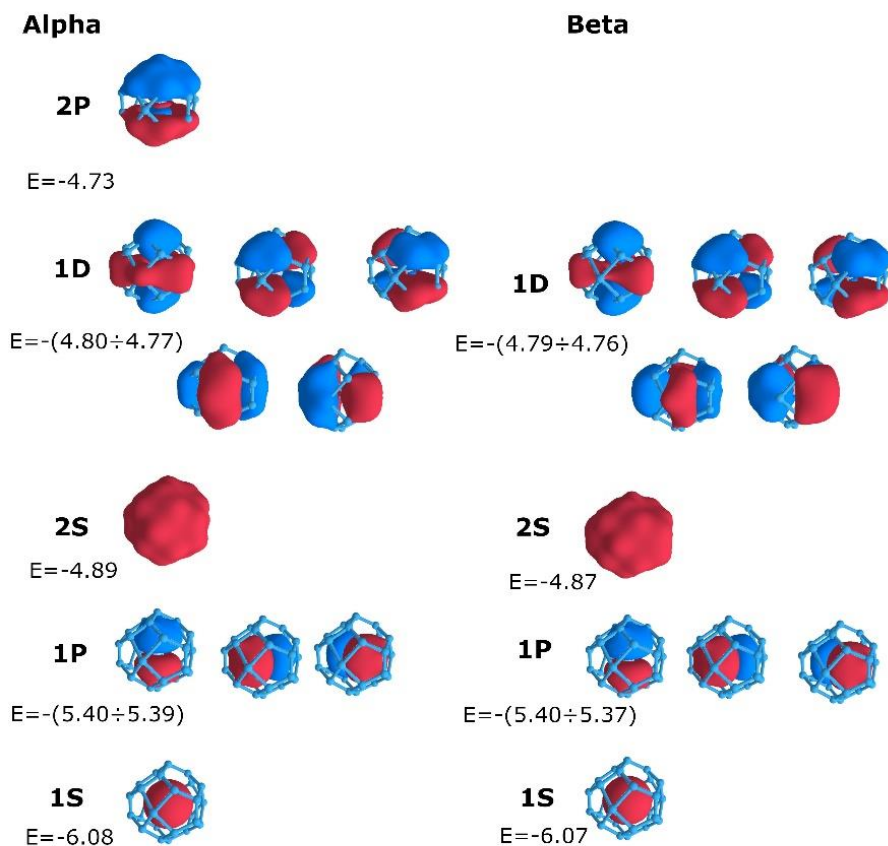


Figure S18. Molecular orbitals and energies (Hartree) of CeH₂₉²⁰⁺ cluster at 100 GPa.

Table S18. Average Bader charges in the investigated europium polyhydrides at 130 GPa.

	<i>Pm3n</i> -Eu ₈ H ₄₆	<i>F43m</i> -EuH ₉	<i>P6₃/mmc</i> -EuH ₉
Average charge on Eu atoms	+1.066	+1.086	+1.147
Average charge on H atoms	−0.185	−0.121	−0.127

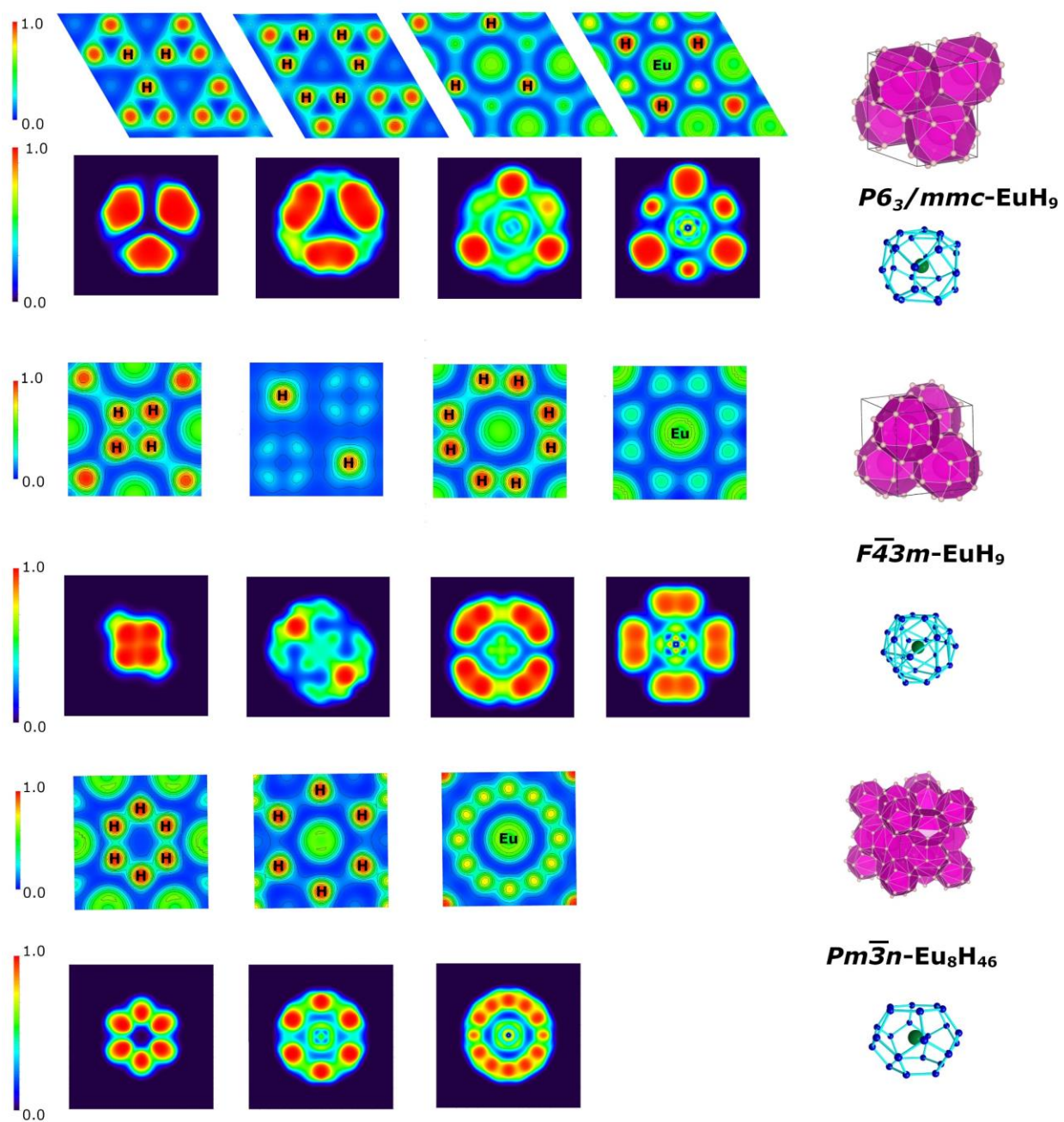


Figure S19. Comparison of the ELF plots of the bulk structures of EuH_9 and Eu_8H_{46} and model clusters at 130 GPa.

Electronic Band Structure

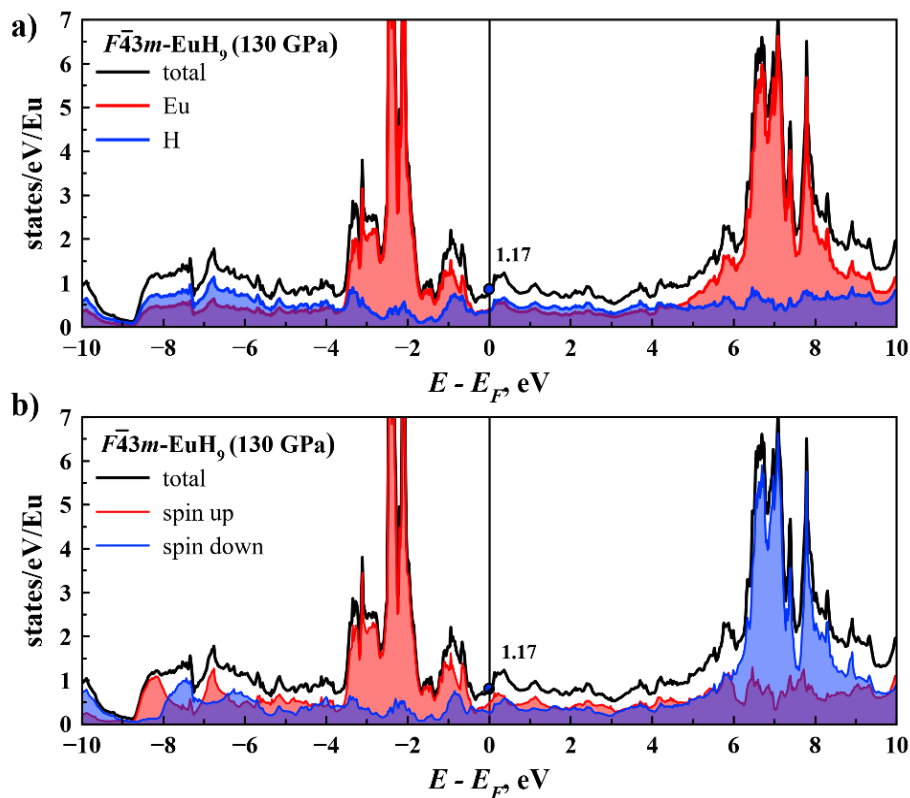


Figure S20. Electron density of states (DOS) of $F\bar{4}3m$ -EuH₉ at 130 GPa per 1 Eu atom (DFT+U). (a) Contributions of the Eu and H atoms to the total DOS. (b) Contributions of different spin orientations to the total DOS.

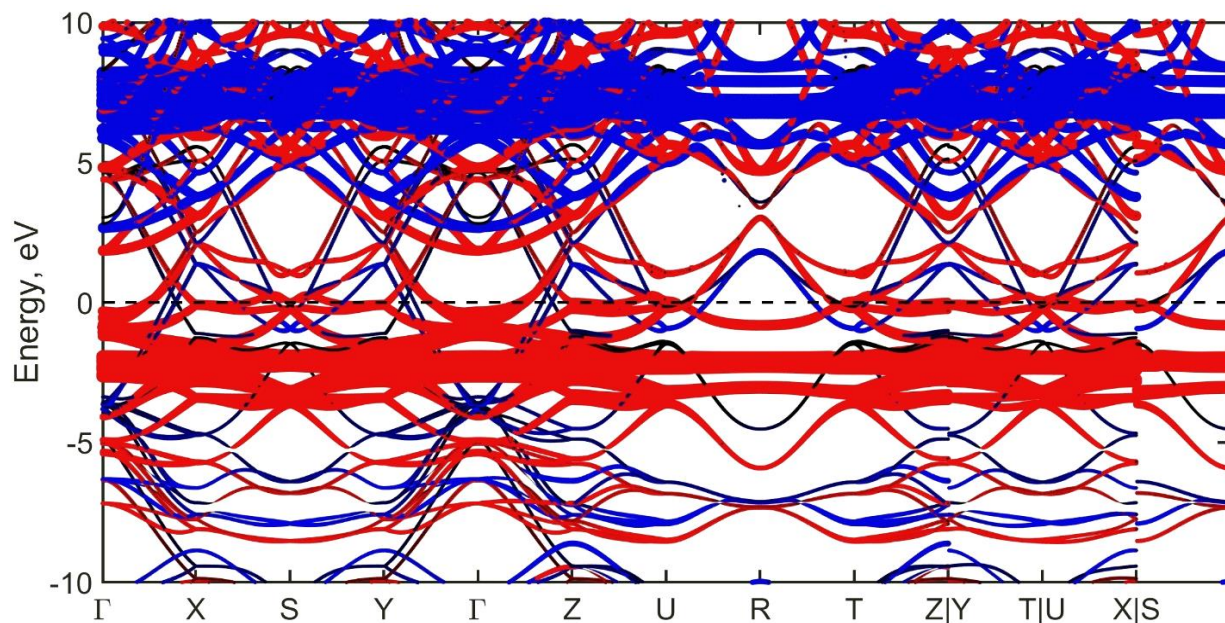


Figure S21. Spin-resolved electron band structure (DFT+U) of $F\bar{4}3m$ -EuH₉ at 130 GPa. Bands of Eu are shown in red (spin up) and blue (spin down), bands of H - in black.

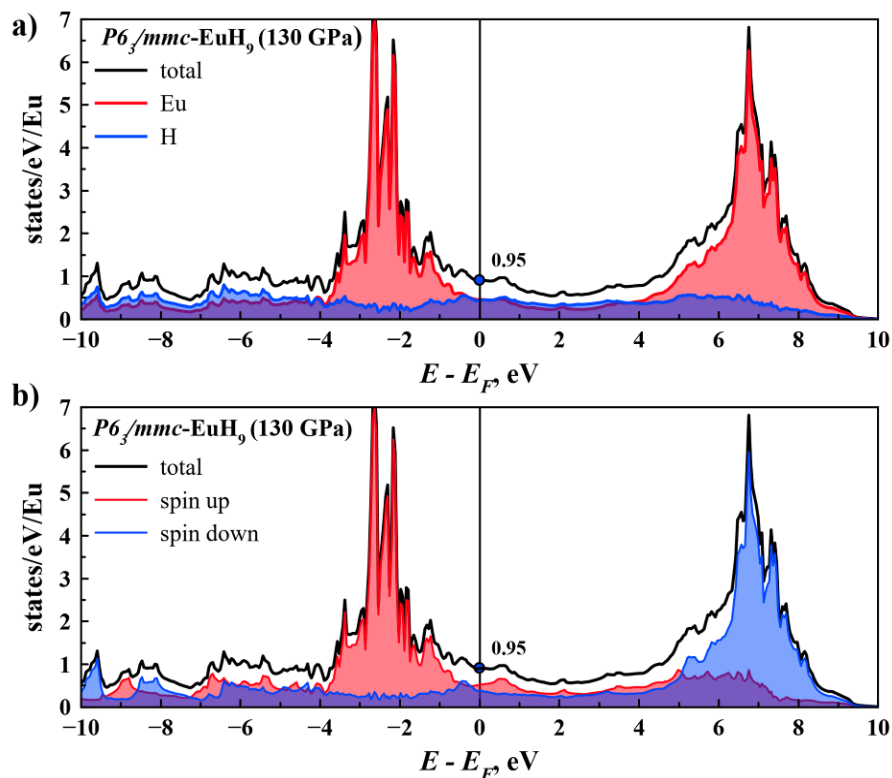


Figure S22. Electron density of states (DOS) of $P6_3/mmc$ -EuH₉ at 130 GPa per 1 Eu atom. (a) Contributions of the Eu and H atoms to the total DOS. (b) Contributions of different spin orientations to the total DOS.

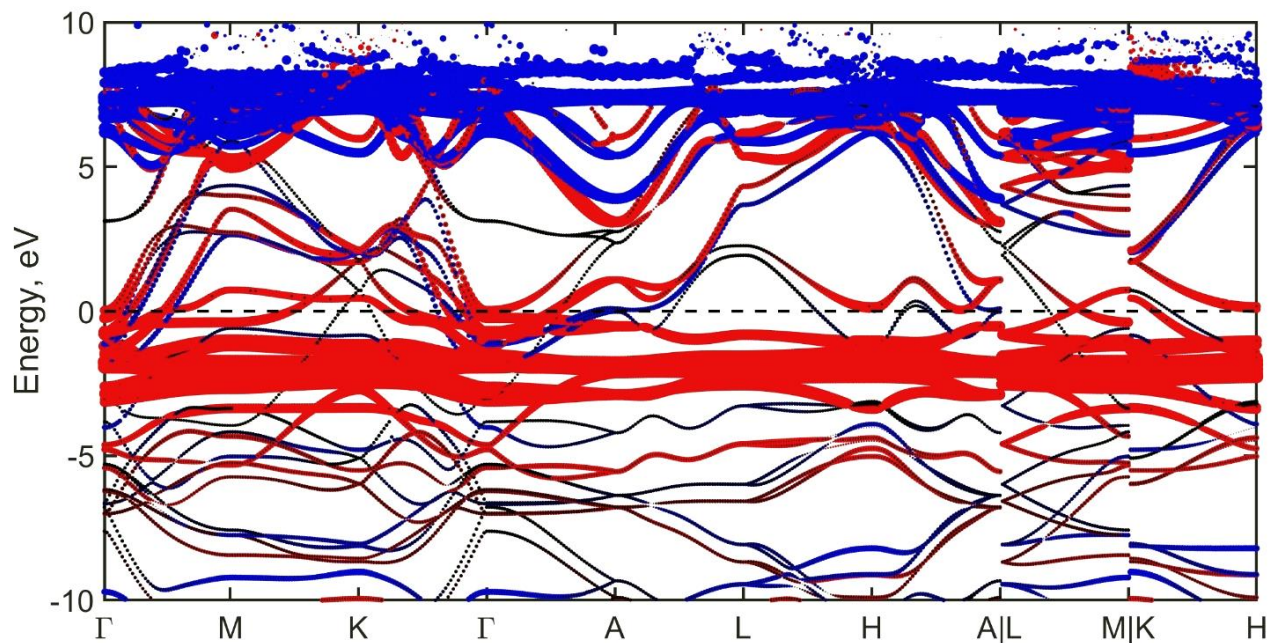


Figure S23. Spin-resolved electron band structure of $P6_3/mmc$ -EuH₉ at 130 GPa. Bands of Eu are shown in red (spin up) and blue (spin down), bands of H presents in black.

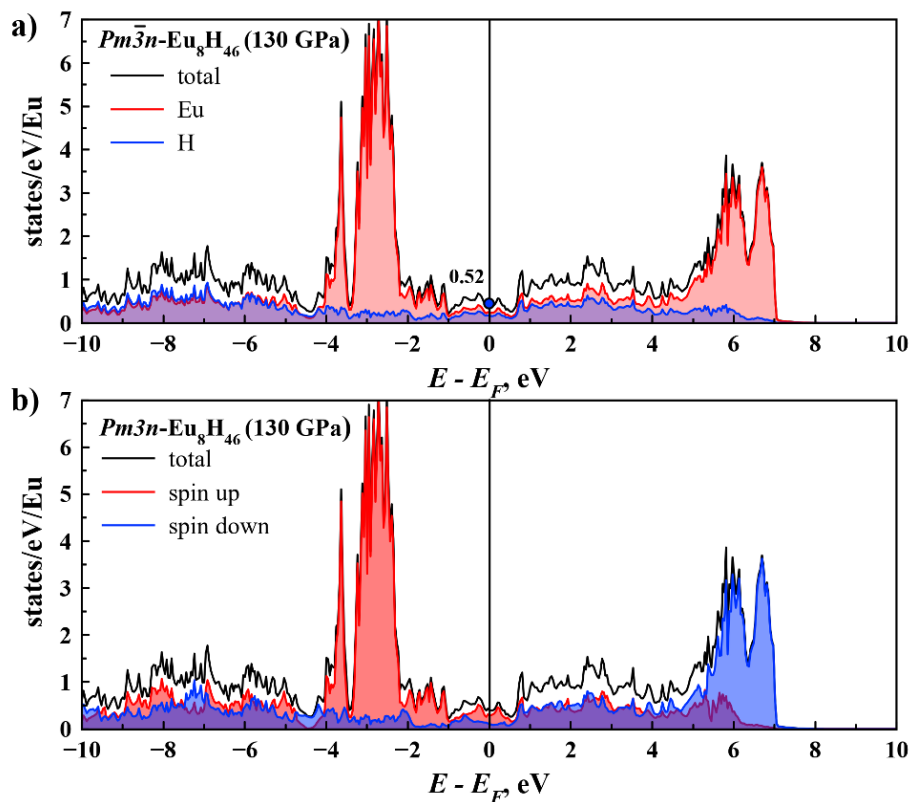


Figure S24. Electron density of states (DOS) of $Pm\bar{3}n$ -Eu₈H₄₆ at 130 GPa per 1 Eu atom. (a) Contributions of the Eu and H atoms to the total DOS. (b) Contributions of different spin orientations to the total DOS.

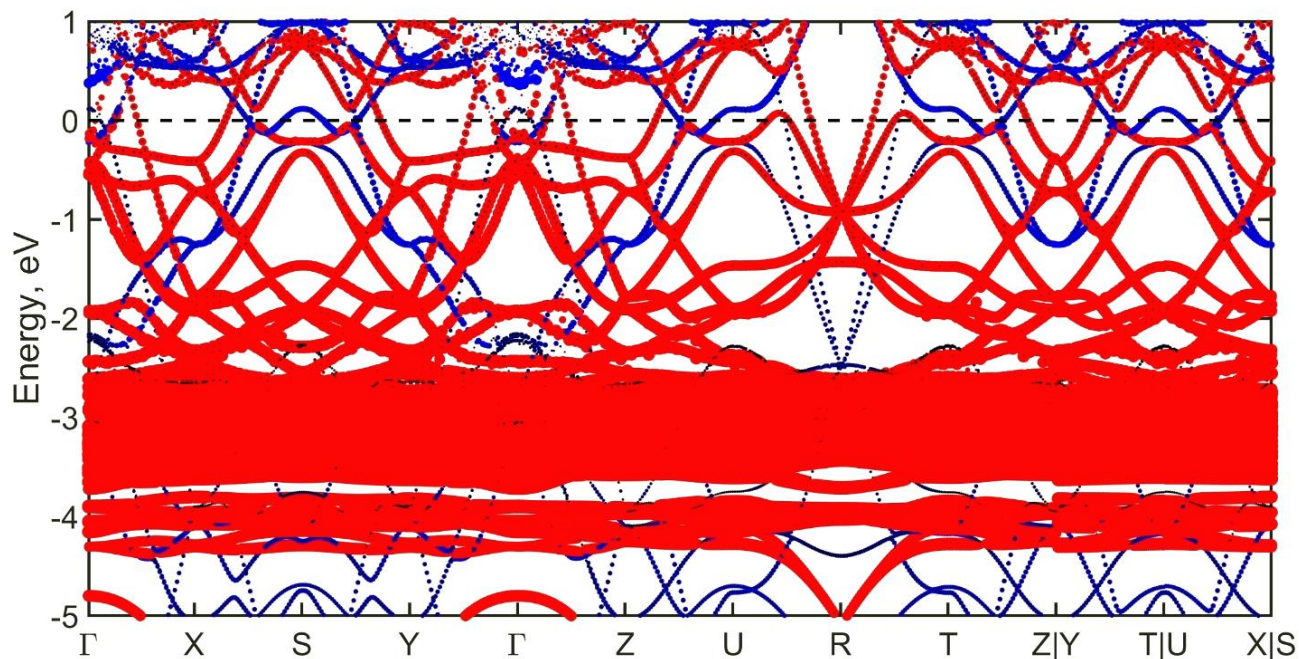


Figure S25. Spin-resolved electron band structure of $Pm\bar{3}n$ -Eu₈H₄₆ at 130 GPa. Bands of Eu are shown in red (spin up) and blue (spin down), bands of H presents in black.

Phonon Spectra

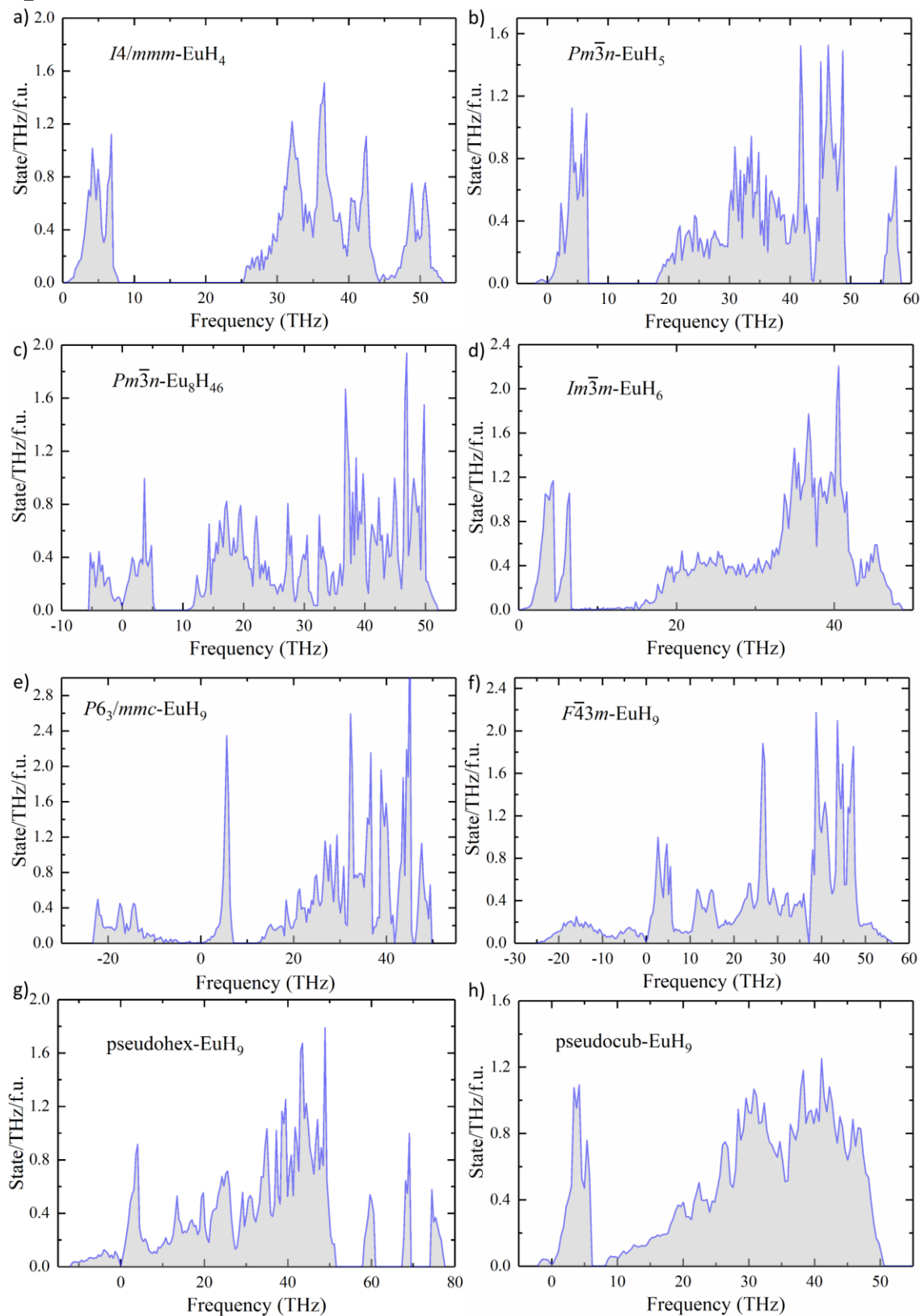


Figure S26. Phonon density of states for various Eu-H phases at 130 GPa with SOC and corresponding U - J (Table S7). Almost all spectra have an imaginary part associated with the distortion of ideal high-symmetry structures or with bad convergence within the selected pseudopotentials. Ideal EuH₉ phases are unstable, whereas distorted $P1$ -EuH₉ has much smaller number of imaginary frequencies. Ideal $Pm\bar{3}n$ -Eu₈H₄₆ also undergoes distortion.

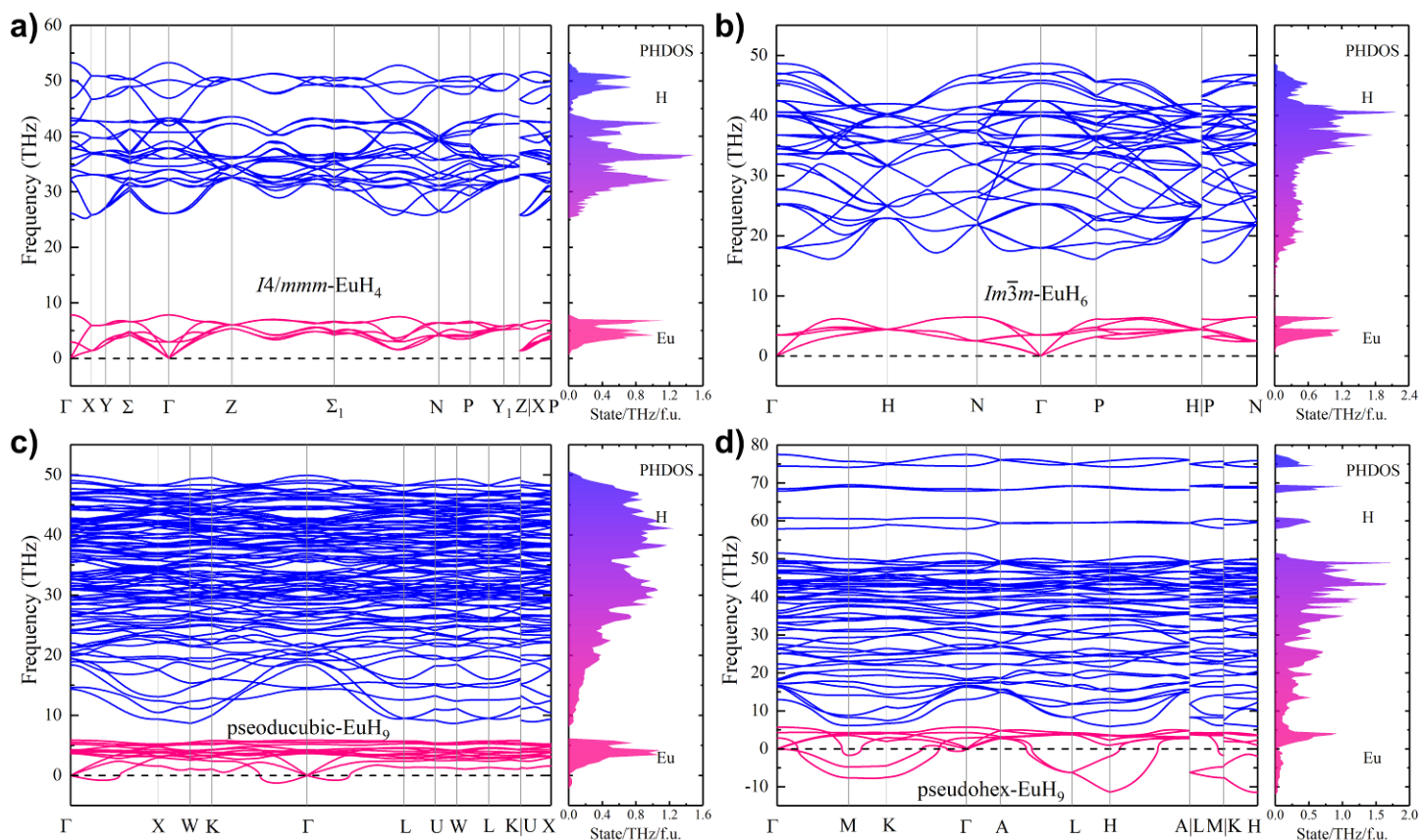


Figure S27. Phonon band structure of various Eu hydrides at 130 GPa with SOC and corresponding U – J (Table S7). Almost all spectra have an imaginary part associated with distortion of ideal high-symmetry structures or with bad convergence within the selected PPs.

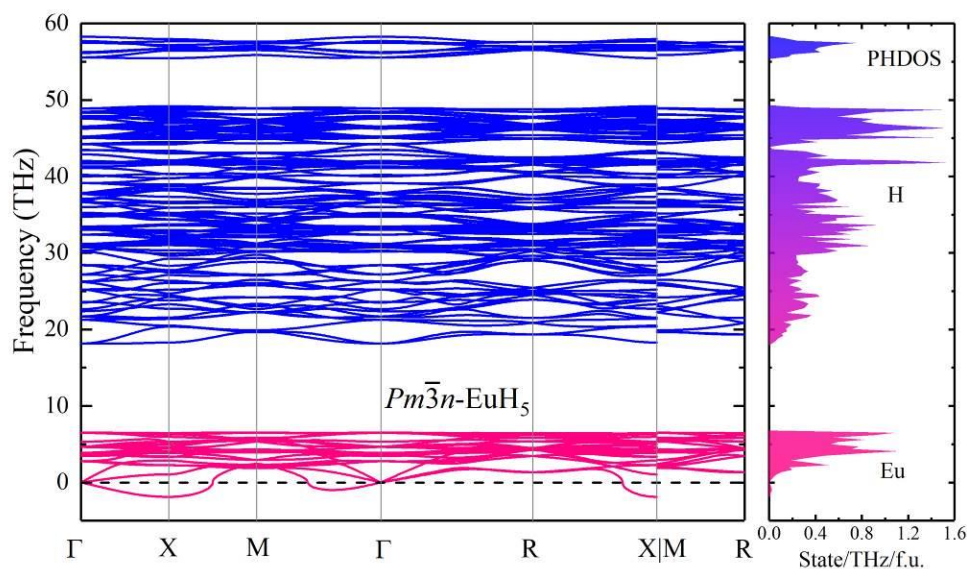


Figure S28. Phonon band structure of $Pm\bar{3}n$ -EuH₅ at 130 GPa with SOC and corresponding U – J (Table S7).

Anharmonic Calculations

The dynamic stability and phonon density of states of the europium hydrides were studied using classical molecular dynamics and interatomic potential based on machine learning. We used the Moment Tensor Potential (MTP).⁴¹ It has been demonstrated that the MTP can be used to calculate the phonon properties of materials.⁴¹ Moreover, within this approach we can explicitly take into account the anharmonicity of hydrogen vibrations.

To train the potential, we first simulated studied europium hydrides in quantum molecular dynamics in an NPT ensemble at 130 GPa and 2000 K, with a duration of 5 picoseconds using the VASP code.^{13–15} We used the PAW PBE pseudopotentials for the H and Eu atoms, $2\pi \times 0.06 \text{ \AA}^{-1}$ k -mesh with a cutoff energy of 400 eV, and a $2 \times 2 \times 1$ supercell with 80 atoms.

For training of the MTP, sets of both EuH_9 and Eu_8H_{46} structures were chosen using active learning.⁴² We checked the dynamical stability of studied europium hydrides with the obtained MTPs via several runs of molecular dynamics calculations at 300 K and 130 GPa. First, the NPT dynamics simulations were performed in a supercell with 960 atoms for 40 picoseconds. During the last 20 picoseconds, the cell parameters were averaged. At the second step, the coordinates of the atoms were averaged within the NVT dynamics with a duration of 20 picoseconds and the final structure was symmetrized. The space groups of both EuH_9 and Eu_8H_{46} were retained, only the lattice parameters were slightly changed.

Then, for the structures of europium polyhydrides relaxed at 130 GPa and 300 K, the phonon density of states was calculated within the MTP using the velocity autocorrelator (VACF) separately for each type of atoms:⁴³

$$g(\vartheta) = 4 \int_0^\infty \cos(2\pi\vartheta t) \frac{\langle \vartheta(0)\vartheta(t) \rangle}{\langle \vartheta(0)^2 \rangle} dt \quad (\text{S3})$$

where ϑ is the frequency. The calculations were carried out in a $20 \times 20 \times 20$ supercell. The velocity autocorrelator was calculated using molecular dynamics, then the phonon DOS was obtained (Figure S29-31).

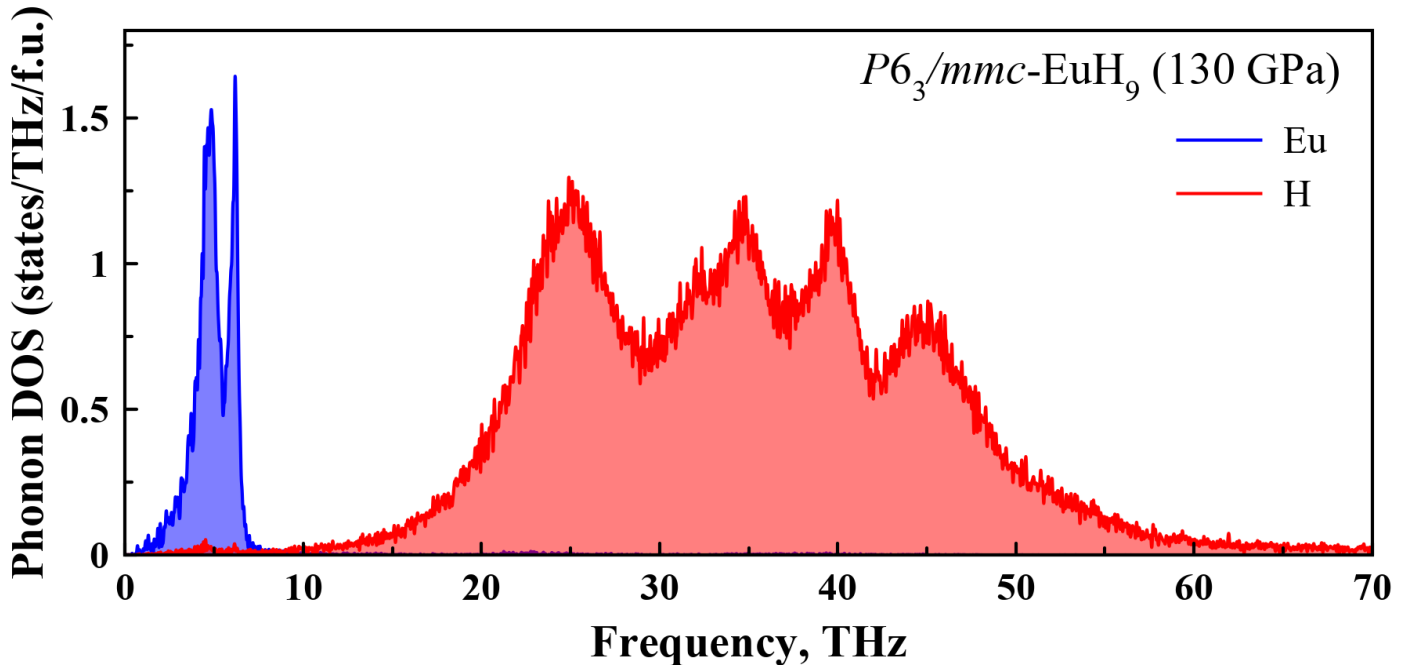


Figure S29. Anharmonic phonon density of states of $P6_3/mmc\text{-EuH}_9$ at 130 GPa and 300 K.

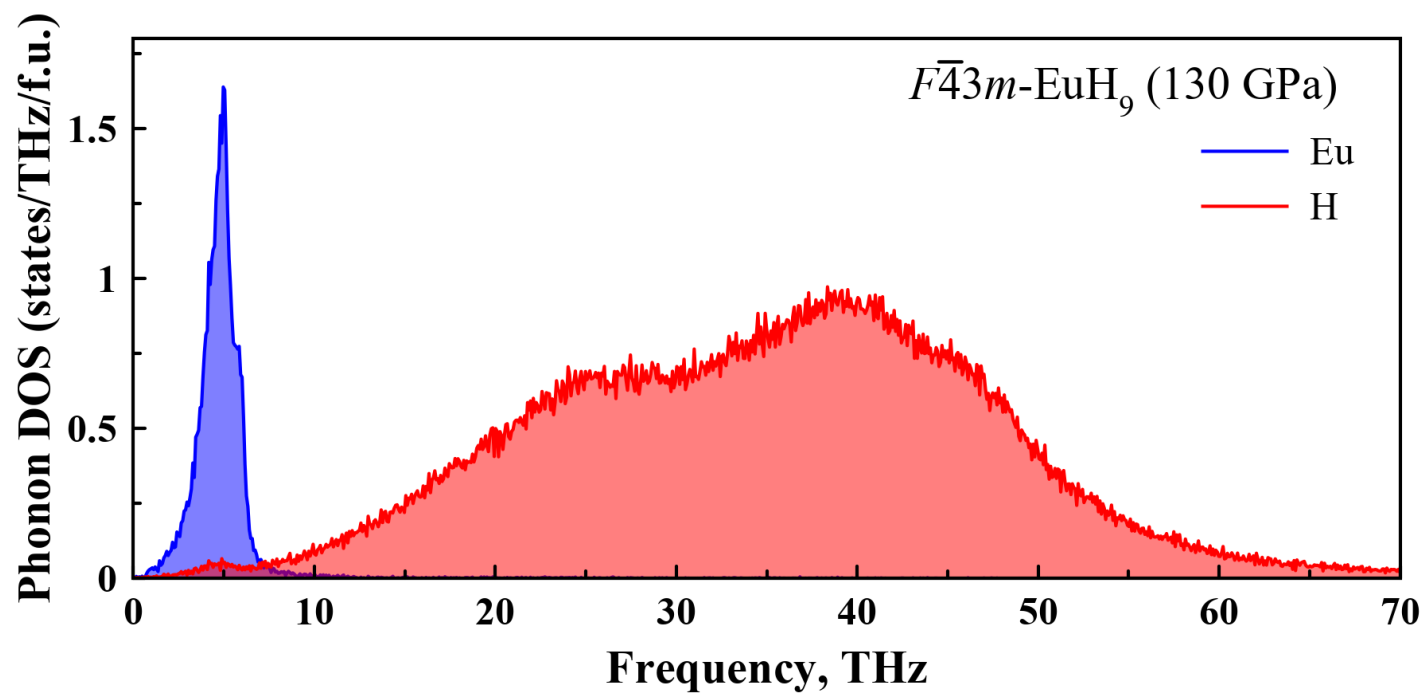


Figure S30. Anharmonic phonon density of states of $F\bar{4}3m$ -EuH₉ at 130 GPa and 300 K.

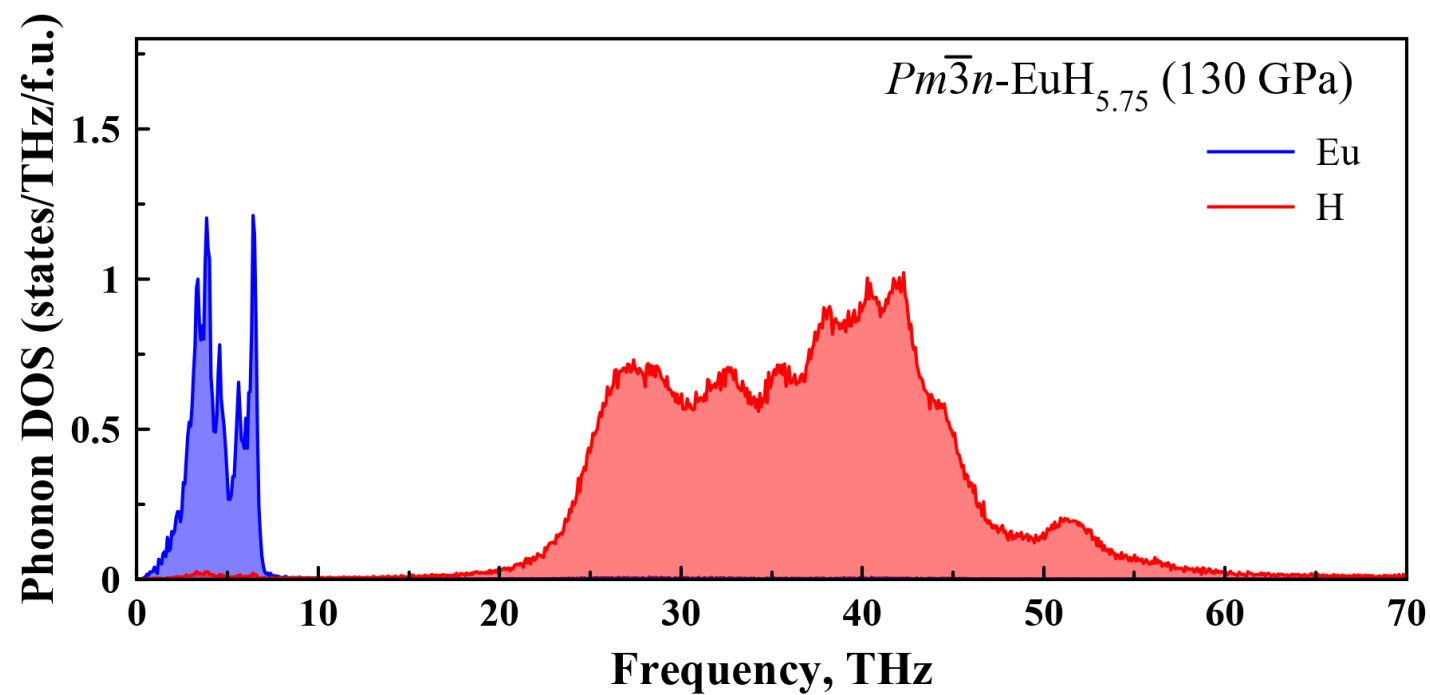


Figure S31. Anharmonic phonon density of states of $Pm\bar{3}n$ -Eu₈H₄₆ at 130 GPa and 300 K.

Elastic Properties of the Eu–H phases

The elastic tensors of the Eu–H phases were calculated using the stress–strain relations:

$$C_{ij} = \frac{\partial \sigma_i}{\partial \eta_j} \quad (\text{S4})$$

where σ_i is the i th component of the stress tensor, η_j is the j th component of the strain tensor.

The bulk and shear moduli B and G and Young's modulus E were calculated in GPa via the Voigt–Reuss–Hill averaging.^{35,36} Using the obtained values of the elastic moduli, we calculated the velocities of longitudinal and transverse acoustic waves:

$$v_{\text{LA}} = \sqrt{\frac{C_{11}}{\rho}}, \quad v_{\text{TA}} = \sqrt{\frac{C_{11} - C_{12}}{2\rho}} \quad (\text{S5})$$

where C_{11} , C_{12} are the elastic constants, ρ is the density of a compound. The obtained values allow us to estimate the Debye temperature:³⁶

$$\vartheta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} v_m \quad (\text{S6})$$

where h , k_B , N_A are the Planck, Boltzmann, and Avogadro constants, and v_m is the average velocity of acoustic waves calculated with the following formula:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_{\text{TA}}^3} + \frac{1}{v_{\text{LA}}^3} \right) \right]^{-1/3} \quad (\text{S7})$$

Table S19. Elastic and thermodynamic parameters of EuH₉ at 130 GPa (SOC+U). To simplify the calculations, ENCUT was reduced to 400–500 eV.

Parameter	$P6_3/mmc$ -EuH ₉	$F\bar{4}3m$ -EuH ₉
a , Å	3.5450	5.009
c , Å	5.9303	-
V_{DFT} , Å ³	32.27	31.41
C_{11} , GPa	466	561
C_{12} , GPa	198	112
C_{13} , GPa	226	112
C_{33} , GPa	439	561
C_{44} , GPa	143	148
B , GPa	297	261
G , GPa	131	175
E , GPa	343	429
Poisson's ratio η	0.307	0.226
Debye temperature θ_D , K	970	987
$\omega_{\text{og}} = 0.827\theta_D$, K	802	817

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