Supplemental Material for "Stabilization of Metallic, Excitonic Insulator, and Superionic Phases in Helium–Rare Gas Compounds at Sub-Terapascal Pressures"

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```
Ne2He-I4mcm-1000GPa
 1.0000000000000000
     3.4190928961666476    0.0000000000000000    0.0000000000000000
     0.0000000000000000    3.4190928961666476    0.0000000000000000
     0.0000000000000000    0.0000000000000000    2.7770572911866127
 Ne  He
  8   4
Direct
  0.1631513028387973  0.3368486971612026  0.5000000000000000
  0.8368486971612026  0.6631513028387973  0.5000000000000000
  0.1631513028387973  0.6631513028387973  0.0000000000000000
  0.8368486971612026  0.3368486971612026  0.0000000000000000
  0.6631513028387973  0.8368486971612026  0.0000000000000000
  0.3368486971612028  0.1631513028387972  0.0000000000000000
  0.6631513028387973  0.1631513028387972  0.5000000000000000
  0.3368486971612028  0.8368486971612026  0.5000000000000000
  0.0000000000000000  0.0000000000000000  0.7500000000000001
  0.0000000000000000  0.0000000000000000  0.2500000000000000
  0.4999999999999999  0.4999999999999999  0.2500000000000000
  0.4999999999999999  0.4999999999999999  0.7500000000000001
```

Supplementary Figure 1: Crystal structure (`VASP` file format, direct coordinates) of Ne_2He in the tetragonal $I4/mcm$ phase at a pressure of approximately $1,000$ GPa.

```
NeHe2-P6_3mmmc-10GPa
 1.0000000000000000
     4.1822724292920341    0.0000000000000000    0.0000000000000000
    -2.0911362146460171    3.6219541693141588    0.0000000000000000
     0.0000000000000000    0.0000000000000000    6.8213310503601639
 Ne  He
  4   8
Direct
  0.3333333333333333  0.6666666666666666  0.5628018316853414
  0.6666666666666667  0.3333333333333333  0.0628018316853414
  0.3333333333333333  0.6666666666666667  0.9371981683146585
  0.6666666666666667  0.3333333333333334  0.4371981683146586
  0.8308958411536480  0.1691041588463520  0.7500000000000000
  0.1691041588463520  0.3382083176927040  0.2500000000000000
  0.6617916823072961  0.8308958411536481  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.5000000000000000
  0.8308958411536481  0.6617916823072961  0.7500000000000000
  0.1691041588463520  0.8308958411536481  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  0.3382083176927040  0.1691041588463520  0.7500000000000000
```

Supplementary Figure 2: Crystal structure (`VASP` file format, direct coordinates) of $NeHe_2$ in the hexagonal $P6_3/mmc$ phase at a pressure of approximately 10 GPa.

```
NeHe2-Fd-3m-10GPa
 1.0000000000000000
     5.9132481978144620    0.0000000000000000    0.0000000000000000
     0.0000000000000000    5.9132481978144620    0.0000000000000000
     0.0000000000000000    0.0000000000000000    5.9132481978144620
 Ne  He
  8  16
Direct
  0.2500000000000000  0.7500000000000001  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.5000000000000000
  0.2500000000000000  0.2500000000000000  0.7500000000000001
  0.0000000000000000  0.5000000000000000  0.0000000000000000
  0.7500000000000001  0.7500000000000001  0.7500000000000001
  0.5000000000000000  0.0000000000000000  0.0000000000000000
  0.7500000000000001  0.2500000000000000  0.2500000000000000
  0.5000000000000000  0.5000000000000000  0.5000000000000000
  0.1250000000000000  0.1250000000000000  0.1250000000000000
  0.8750000000000000  0.8750000000000000  0.1250000000000000
  0.6250000000000000  0.8750000000000000  0.3750000000000001
  0.3750000000000001  0.1250000000000000  0.3750000000000001
  0.1250000000000000  0.6250000000000000  0.6250000000000000
  0.8750000000000000  0.3750000000000001  0.6250000000000000
  0.6250000000000000  0.3750000000000001  0.8750000000000000
  0.3750000000000001  0.6250000000000000  0.8750000000000000
  0.6250000000000000  0.1250000000000000  0.6250000000000000
  0.3750000000000001  0.8750000000000000  0.6250000000000000
  0.1250000000000000  0.8750000000000000  0.8750000000000000
  0.8750000000000000  0.1250000000000000  0.8750000000000000
  0.6250000000000000  0.6250000000000000  0.1250000000000000
  0.3750000000000001  0.3750000000000001  0.1250000000000000
  0.1250000000000000  0.3750000000000001  0.3750000000000001
  0.8750000000000000  0.6250000000000000  0.3750000000000001
```

Supplementary Figure 3: Crystal structure (`VASP` file format, direct coordinates) of $NeHe_2$ in the cubic $Fd\bar{3}m$ phase at a pressure of approximately 10 GPa.

```
Ar2He-I4mcm-1000GPa
 1.0000000000000000
     3.9203412008975373    0.0000000000000000    0.0000000000000000
     0.0000000000000000    3.9203412008975373    0.0000000000000000
     0.0000000000000000    0.0000000000000000    3.3153908966306909
 Ar  He
  8   4
Direct
  0.1682019676701003  0.6682019676701003  0.0000000000000000
  0.1682019676701003  0.3317980323298997  0.4999999999999999
  0.3317980323298997  0.8317980323298997  0.4999999999999999
  0.3317980323298997  0.1682019676701003  0.0000000000000000
  0.6682019676701003  0.1682019676701003  0.4999999999999999
  0.6682019676701003  0.8317980323298997  0.0000000000000000
  0.8317980323298997  0.3317980323298997  0.0000000000000000
  0.8317980323298997  0.6682019676701003  0.4999999999999999
  0.0000000000000000  0.0000000000000000  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.7500000000000000
  0.5000000000000000  0.5000000000000000  0.7500000000000000
  0.5000000000000000  0.5000000000000000  0.2500000000000000
```

Supplementary Figure 4: Crystal structure (`VASP` file format, direct coordinates) of Ar_2He in the tetragonal $I4/mcm$ phase at a pressure of approximately $1,000$ GPa.

```
ArHe-Cmcm-50GPa
 1.0000000000000000
     3.1320993418270957    0.0000000000000000    0.0000000000000000
     0.0000000000000000    8.3357034702823736    0.0000000000000000
     0.0000000000000000    0.0000000000000000    2.9970282450991239
 Ar  He
  4   4
Direct
  0.5000000000000000  0.1459067570395973  0.7500000000000000
  0.0000000000000000  0.3540932429604027  0.2500000000000000
  0.0000000000000000  0.6459067570395973  0.7500000000000000
  0.5000000000000000  0.8540932429604027  0.2500000000000000
  0.5000000000000000  0.4376596194862756  0.7500000000000000
  0.0000000000000000  0.0623403805137244  0.2500000000000000
  0.0000000000000000  0.9376596194862756  0.7500000000000000
  0.5000000000000000  0.5623403805137243  0.2500000000000000
```

Supplementary Figure 5: Crystal structure (`VASP` file format, direct coordinates) of ArHe in the orthorhombic *Cmcm* phase at a pressure of approximately 50 GPa.

```
ArHe-Pnma-300GPa
 1.0000000000000000
     4.8156044012026538    0.0000000000000000    0.0000000000000000
     0.0000000000000000    2.4900117644336008    0.0000000000000000
     0.0000000000000000    0.0000000000000000    3.7146988729780781
 Ar  He
  4   4
Direct
  0.3230355319854894  0.7500000000000000  0.3730998573115016
  0.8230355319854894  0.7500000000000000  0.1269001426884984
  0.6769644680145106  0.2500000000000000  0.6269001426884984
  0.1769644680145106  0.2500000000000000  0.8730998573115017
  0.9682741997051282  0.7500000000000000  0.6084123933595293
  0.4682741997051281  0.7500000000000000  0.8915876066404707
  0.0317258002948718  0.2500000000000000  0.3915876066404707
  0.5317258002948718  0.2500000000000000  0.1084123933595293
```

Supplementary Figure 6: Crystal structure (`VASP` file format, direct coordinates) of ArHe in the orthorhombic *Pnma* phase at a pressure of approximately 300 GPa.

```
ArHe2-P6mmm-200GPa
 1.0000000000000000
     2.5788301551966875    0.0000000000000000    0.0000000000000000
    -1.2894150775983437    2.2333324264456977    0.0000000000000000
     0.0000000000000000    0.0000000000000000    2.6724842885590956
 Ar  He
   1   2
Direct
  0.0000000000000000  0.0000000000000000  0.5000000000000000
  0.6666666666666666  0.3333333333333334  0.0000000000000000
  0.3333333333333334  0.6666666666666669  0.0000000000000000
```

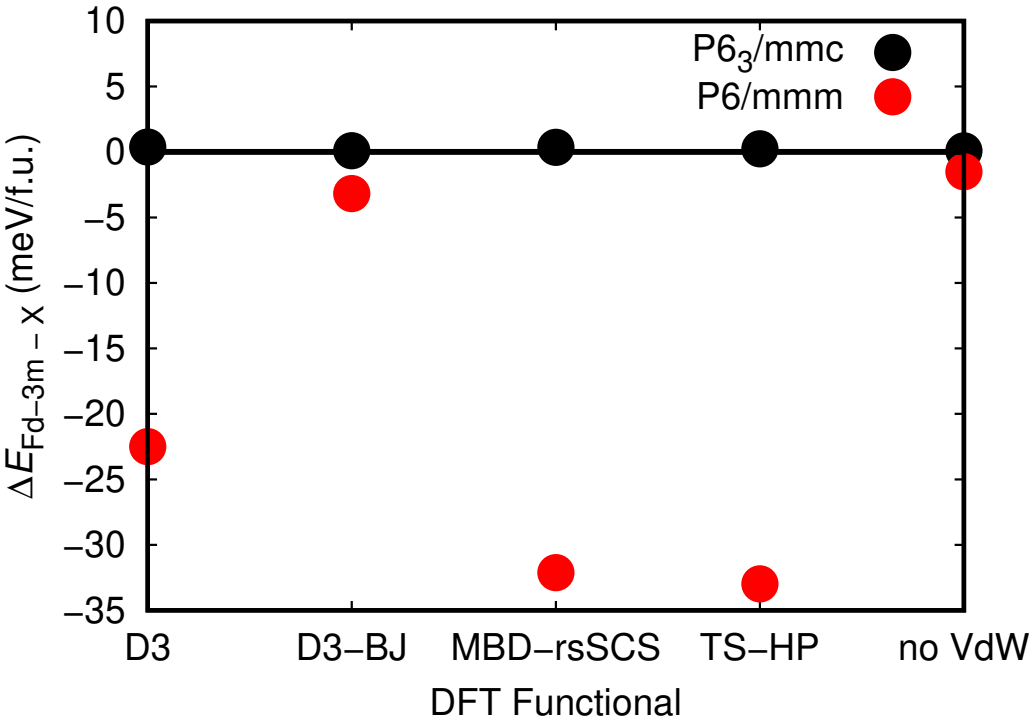
Supplementary Figure 7: Crystal structure (`VASP` file format, direct coordinates) of $ArHe_2$ in the hexagonal $P6/mmm$ phase at a pressure of approximately 200 GPa.

```
XeHe-P63mmc-500GPa
 1.0000000000000000
     2.7258301222343935    0.0000000000000000    0.0000000000000000
    -1.3629150611171967    2.3606381322558261    0.0000000000000000
     0.0000000000000000    0.0000000000000000    4.3361005444398817
 Xe  He
  2   2
Direct
  0.3333333333333333  0.6666666666666666  0.7500000000000000
  0.6666666666666667  0.3333333333333334  0.2500000000000000
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  0.0000000000000000  0.0000000000000000  0.5000000000000000
```

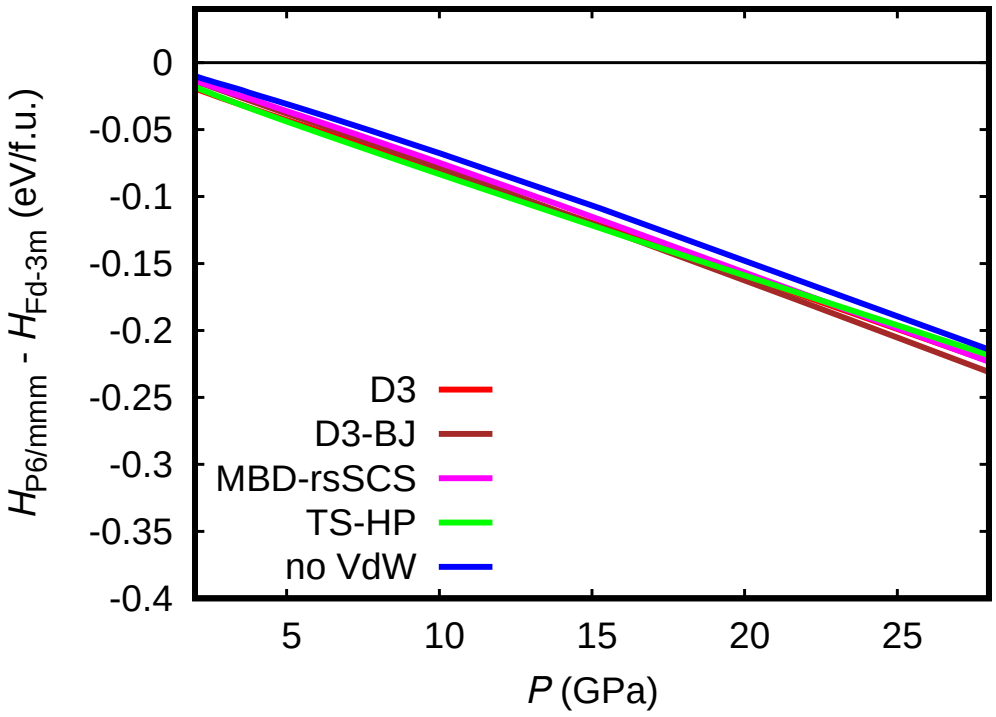
Supplementary Figure 8: Crystal structure (`VASP` file format, direct coordinates) of XeHe in the hexagonal $P6_3/mmc$ phase at a pressure of approximately 500 GPa.

```
XeHe-Fm-3m-1000GPa
 1.0000000000000000
     3.5367610804356175    0.0000000000000000    0.0000000000000000
     0.0000000000000000    3.5367610804356175    0.0000000000000000
     0.0000000000000000    0.0000000000000000    3.5367610804356175
 Xe  He
  4   4
Direct
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  0.0000000000000000  0.4999999999999999  0.4999999999999999
  0.4999999999999999  0.0000000000000000  0.4999999999999999
  0.4999999999999999  0.4999999999999999  0.0000000000000000
  0.4999999999999999  0.0000000000000000  0.0000000000000000
  0.4999999999999999  0.4999999999999999  0.4999999999999999
  0.0000000000000000  0.0000000000000000  0.4999999999999999
  0.0000000000000000  0.4999999999999999  0.0000000000000000
```

Supplementary Figure 9: Crystal structure (`VASP` file format, direct coordinates) of XeHe in the cubic $Fm\bar{3}m$ phase at a pressure of approximately $1,000$ GPa.



Supplementary Figure 10: Zero-temperature energy differences caculated for $ArHe_2$ adopting different polymorphs and considering different DFT exchange-correlation functionals (see Supplementary Discussion).



Supplementary Figure 11: Zero-temperature enthalpy differences caculated for $ArHe_2$ as a function of pressure and considering different DFT exchange-correlation functionals (see Supplementary Discussion).

SUPPLEMENTARY DISCUSSION

To assess the influence of the employed DFT exchange-correlation functional on the results reported in the main text, we conducted a series of numerical tests for $ArHe_2$ under different pressure conditions. Supplementary Figs. 10 and 11 summarize these results, which are discussed below.

Supplementary Fig. 10 shows that, under zero-pressure and zero-temperature conditions, the enthalpies of the Laves hexagonal $P6_3/mmc$ ($Z = 4$) and cubic $Fd\bar{3}m$ ($Z = 8$) phases are indistinguishable within our numerical accuracy of approximately 1 meV per formula unit. This finding is general and independent of the employed DFT exchange-correlation functional. Specifically, we tested four different van der Waals (vdW) functionals accounting for long-range dispersion interactions: "D3" (Grimme's method with zero damping), "D3-BJ" (Grimme's method with Becke-Johnson damping), "MBD-rsSCS" (many-body dispersion approach), and "TS-HP" (Tkatchenko-Scheffler method with iterative Hirshfeld partitioning). We also considered the effect of completely neglecting vdW interactions ("no vdW" case), which did not alter our conclusions. In contrast, the total energy of the non-Laves hexagonal $P6/mmm$ phase lies significantly below those of the two Laves phases, except when long-range dispersion interactions are omitted.

Supplementary Fig. 11 shows that, under compression and irrespective of the chosen DFT exchange-correlation functional, even when vdW forces are fully neglected, the enthalpy of the non-Laves hexagonal $P6/mmm$ phase remains well below those of the Laves cubic $Fd\bar{3}m$ and hexagonal $P6_3/mmc$ phases (the latter two being indistinguishable within our numerical accuracy). In particular, under pressures of a few tens of GPa, the enthalpy difference between the non-Laves hexagonal $P6/mmm$ and Laves cubic $Fd\bar{3}m$ phases reaches several hundred meV per formula unit. Overall, these numerical tests demonstrate that the conclusions presented in the main text are robust and exhibit only a very weak dependence on the choice of DFT exchange-correlation functional.

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