Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

High-pressure formation and stabilization of binary iridium hydrides

(Supplementary Material)

Patryk Zaleski-Ejgierd [a]

[a] Institute of Physical Chemistry, Polish Academy of Sciences,
ul. M. Kasprzaka 44/52, 02-144, Warszawa, Polska

Table S1. Enthalpy (H=U+pV; U= free energy of the ion-electron system, p= pressure, V= volume) and the harmonic ZPE corrections calculated at 125 GPa for selected species.

Ir (fcc)	H_2 (C2/c)	IrH_3 ($P6_3m$)	IrH_2 (Cmcm)	IrH_2 (Ibam)	
1.227	-1.615	-1.697	-0.824	-0.729	Enthalpy @ 125 GPa [ev / f.u.]
0.044	0.580	0.760	0.520	0.546	ZPE @ 125 GPa [ev / f.u.]

Table S2. The enthalpy difference, ΔH, calculated at 0K with and without the inclusion of the ZPE correction calculated for selected reactions and phase transitions.

ΔH @ 0K (including ZPE)	ΔH @ 0K (no ZPE)	Reaction / Phase transition
-0.122	-0.096	IrH_2 (Cmcm) - IrH_2 (Ibam)
-0.419	-0.341	Ir + H_2 -> IrH_2 (Ibam)
-0.541	-0.437	Ir + H_2 -> IrH_2 (Cmcm)
-0.115	-0.065	IrH_2 + 0.5 H_2 -> IrH_3 ($P6_3m$)

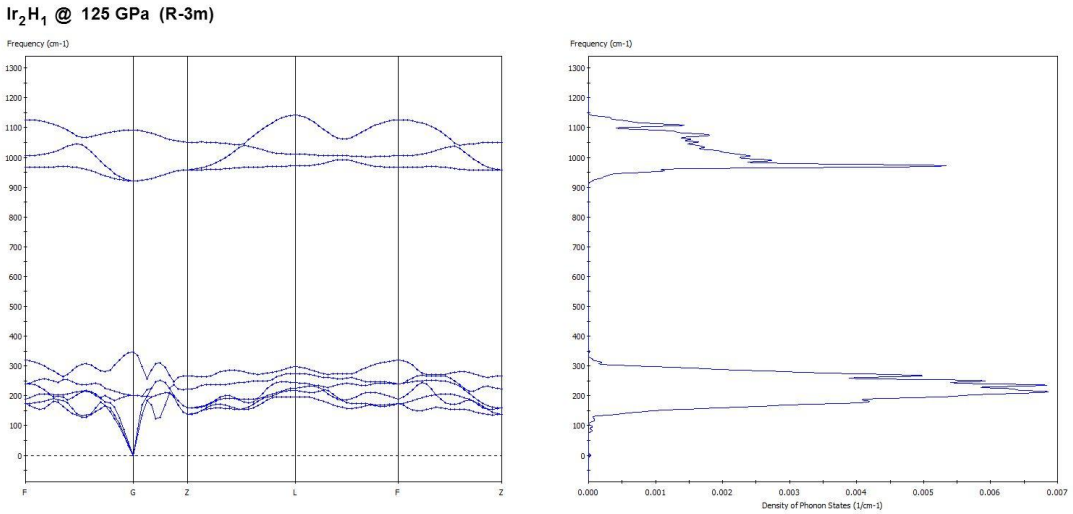

Fig. S1. Phonon dispersions and PhDOS calculated for Ir_2H (R-3m) at 125 GPa.

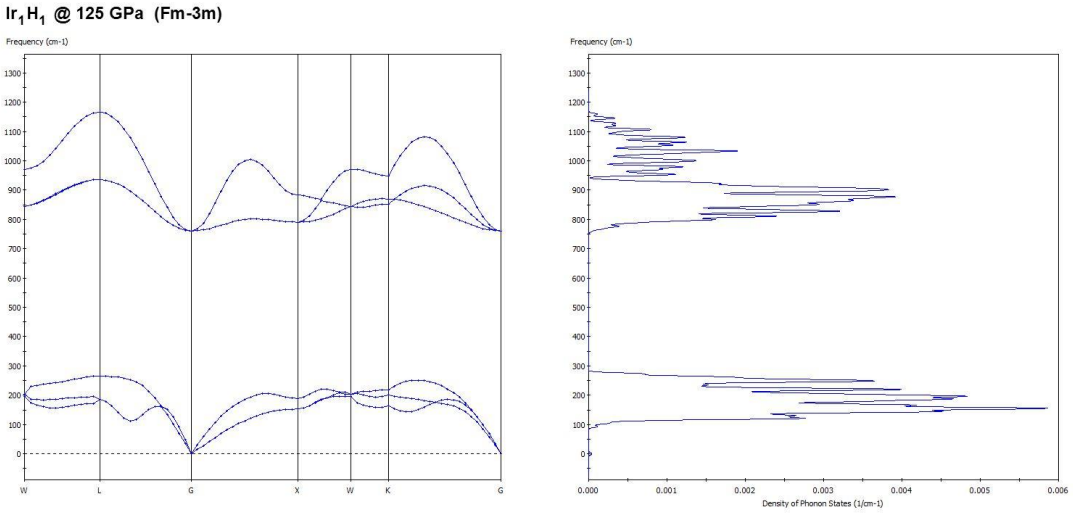

Fig. S2. Phonon dispersions and PhDOS calculated for IrH (Fm-3m) at 125 GPa.

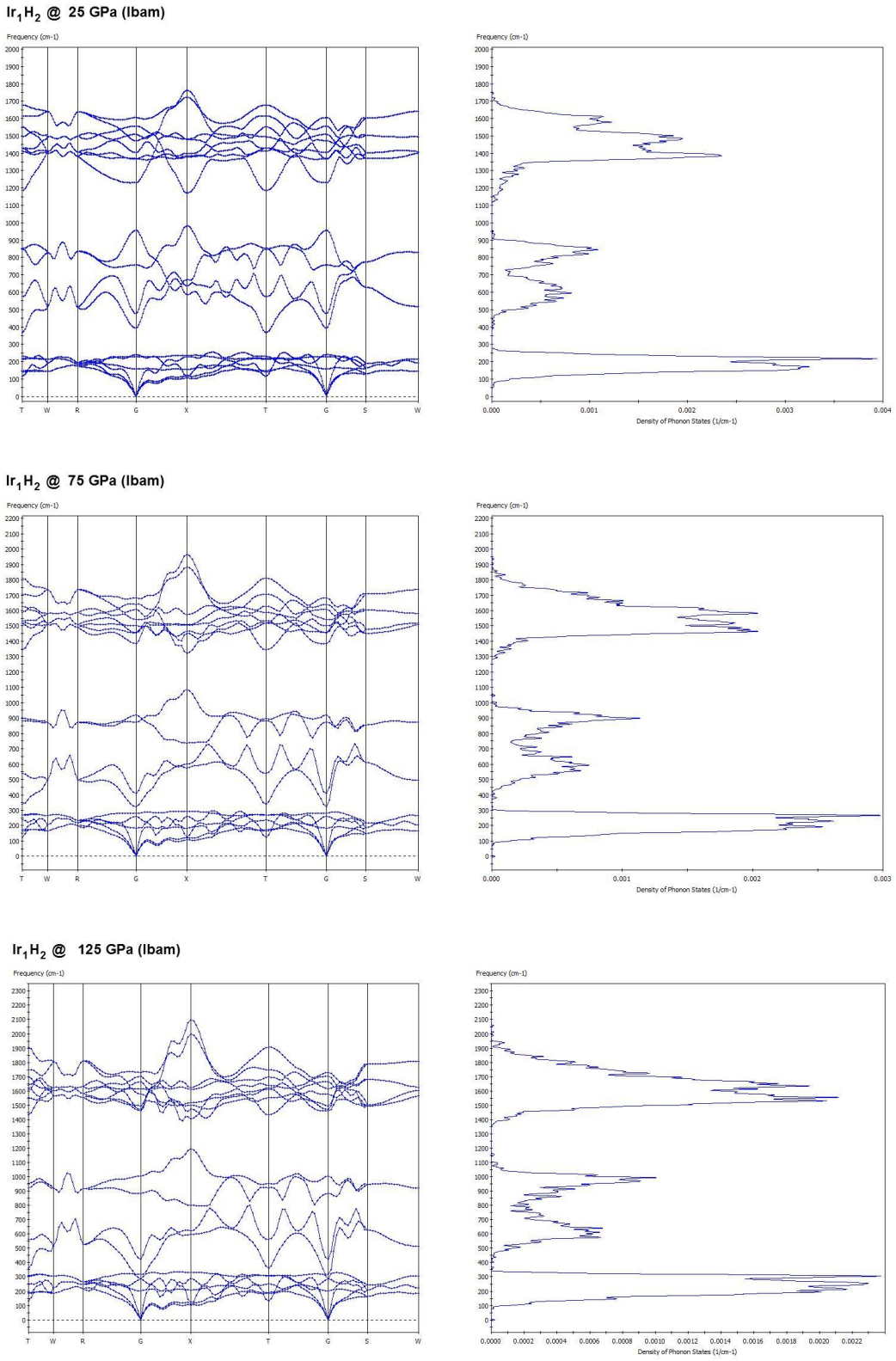

Fig. S3. Phonon dispersions and PhDOS calculated for IrH_2 (Ibam) at 25 (top), 75 (middle) and 125 GPa (bottom).

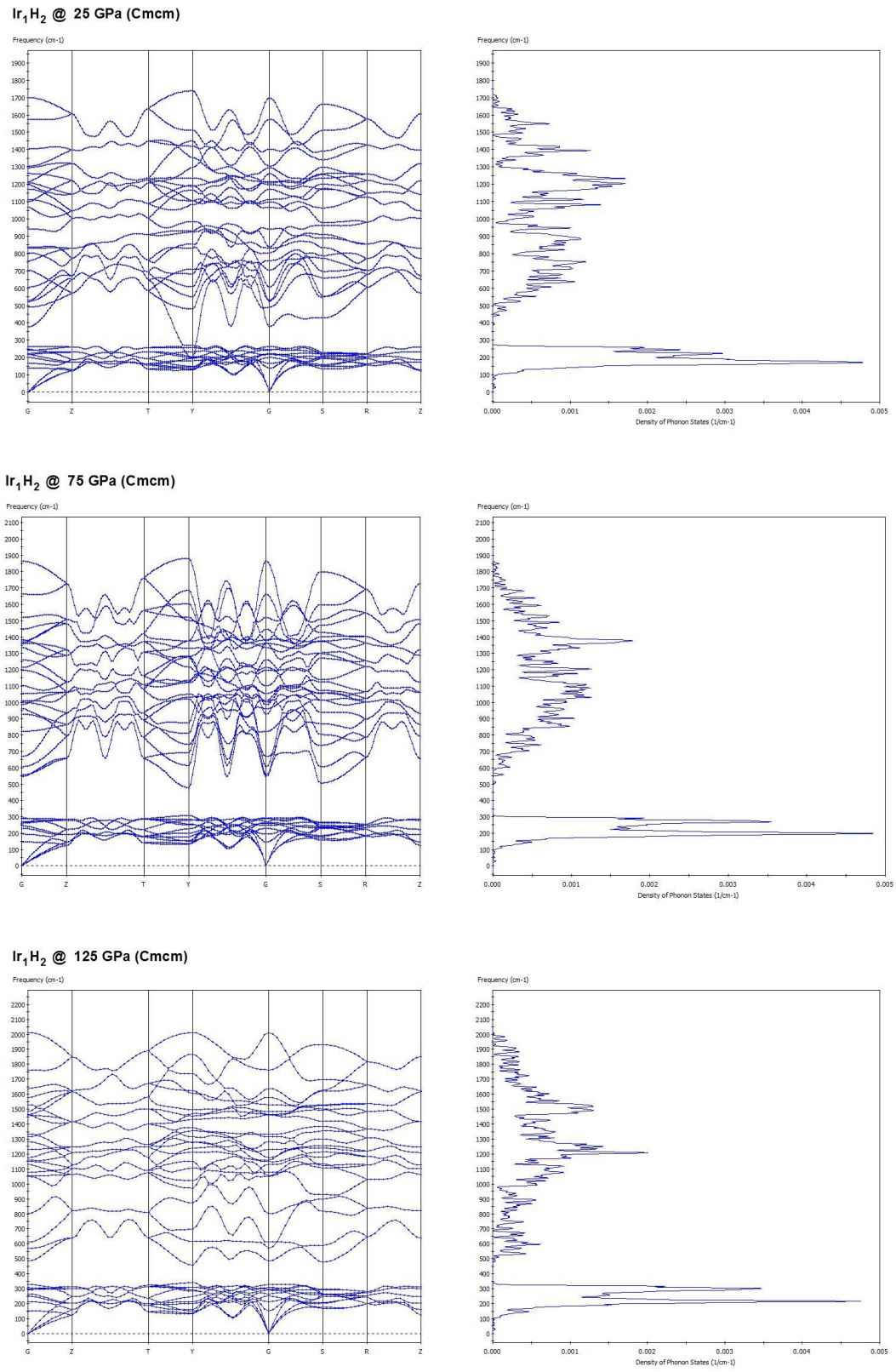

Fig. S4. Phonon dispersions and PhDOS calculated for IrH_2 (Cmcm) at 25 (top), 75 (middle) and 125 GPa (bottom).

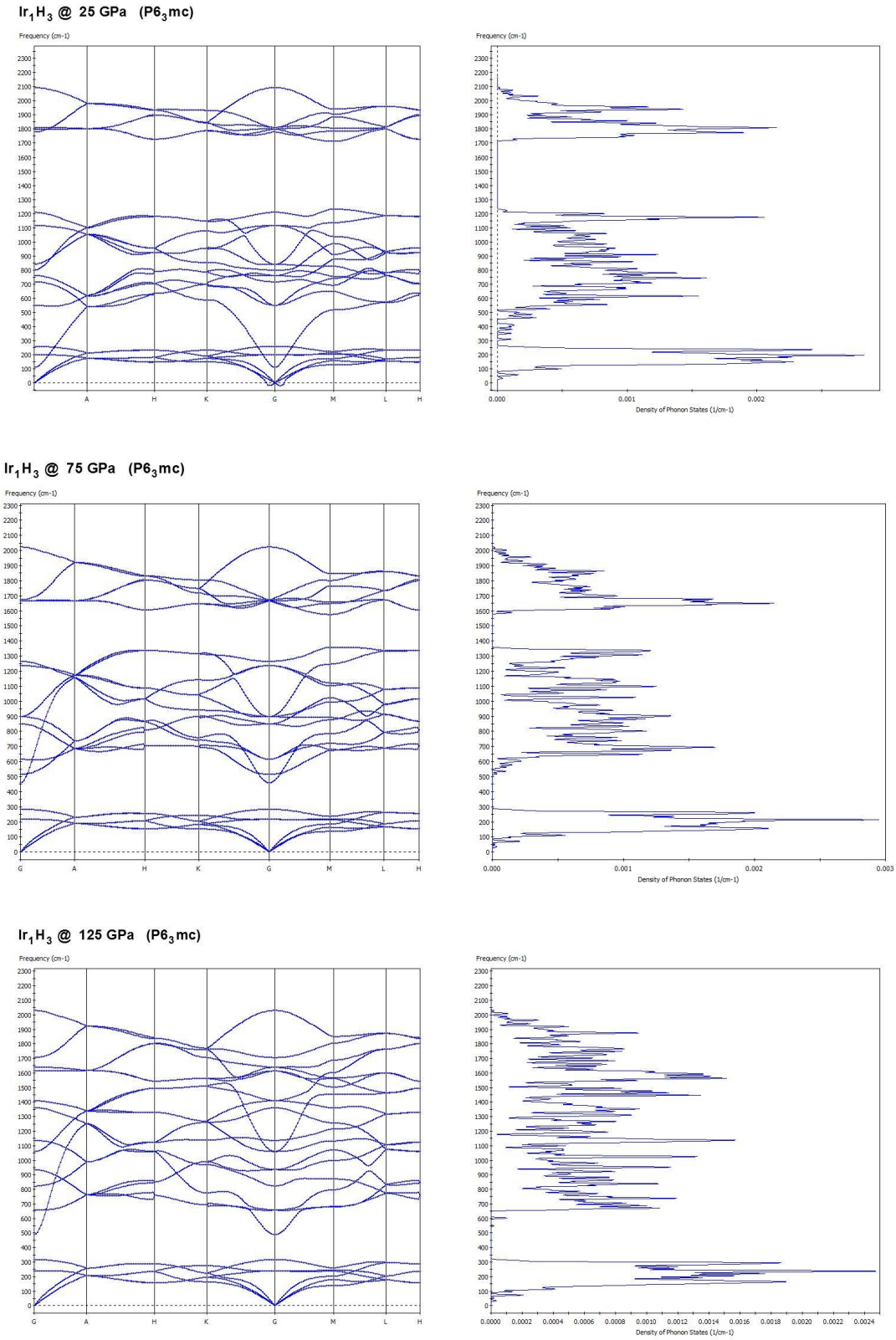

Fig. S5. Phonon dispersions and PhDOS calculated for IrH_3 ($P6_3mc$) at 25 (top), 75 (middle) and 125 GPa (bottom).

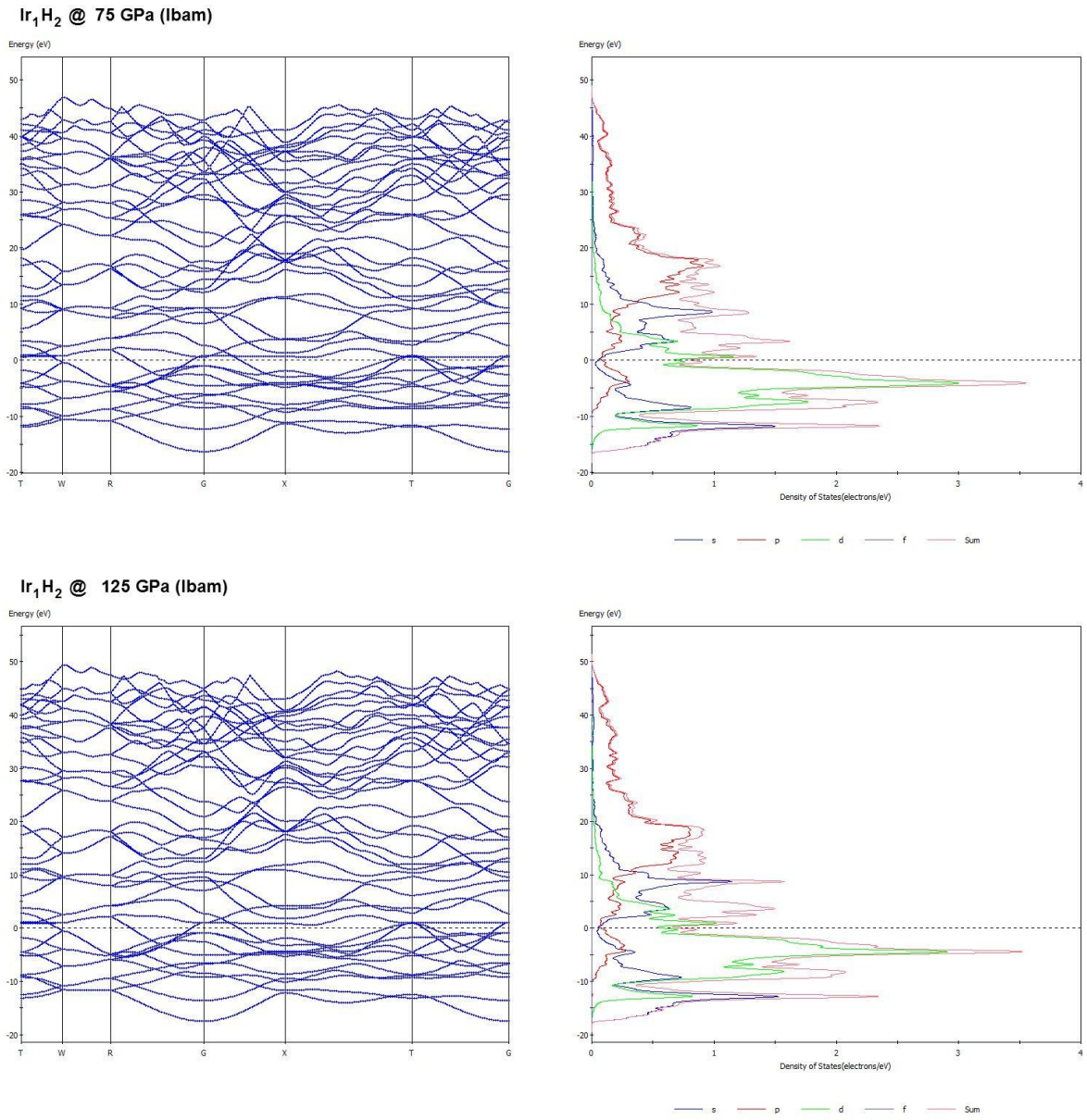

Fig. S6. Band structure and DOS calculated for IrH_2 (Ibam) at 75 (top) and 125 GPa (bottom).

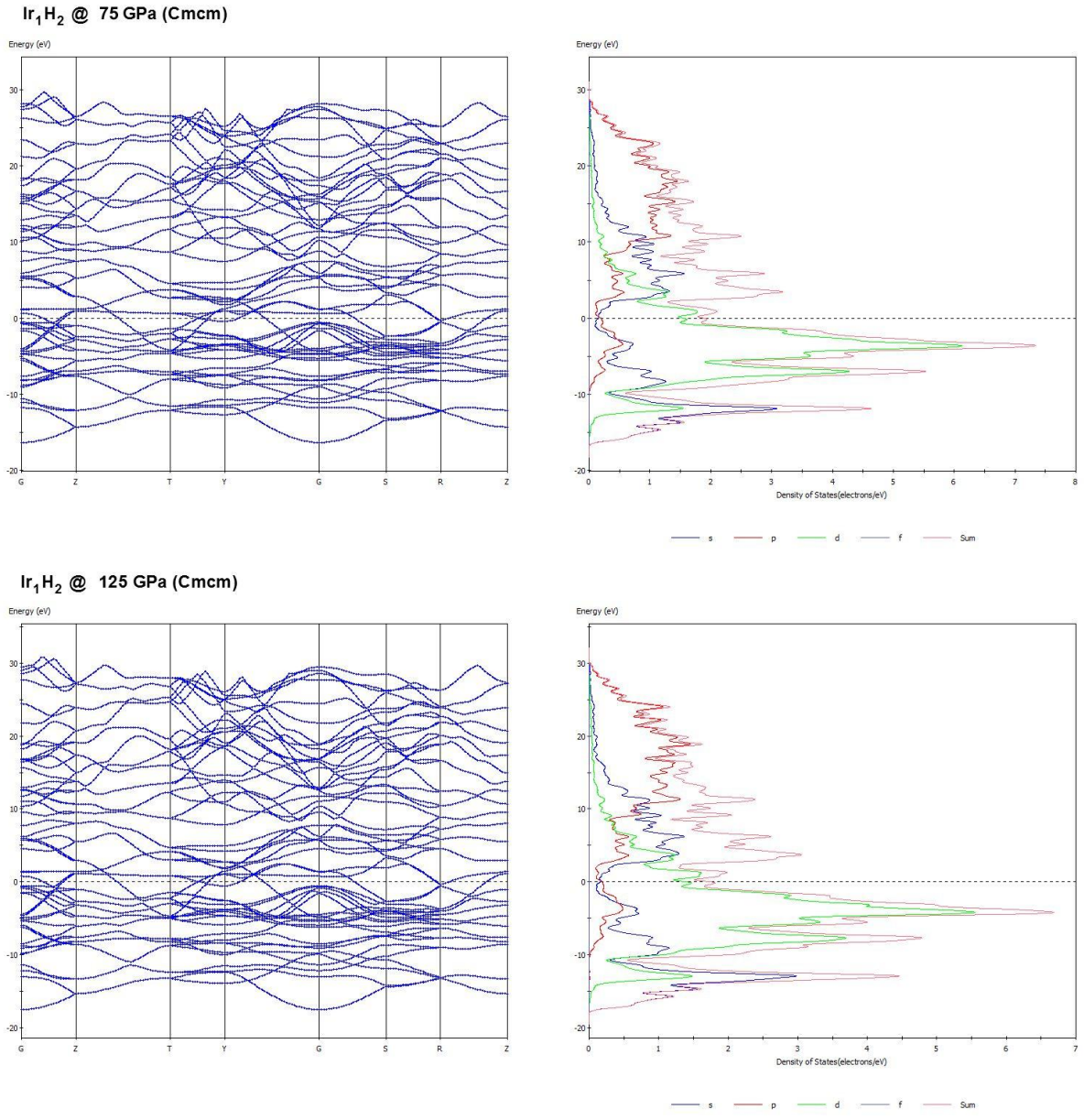

Fig. S7. Band structure and DOS calculated for IrH_2 (Cmcm) at 75 (top) and 125 GPa (bottom).

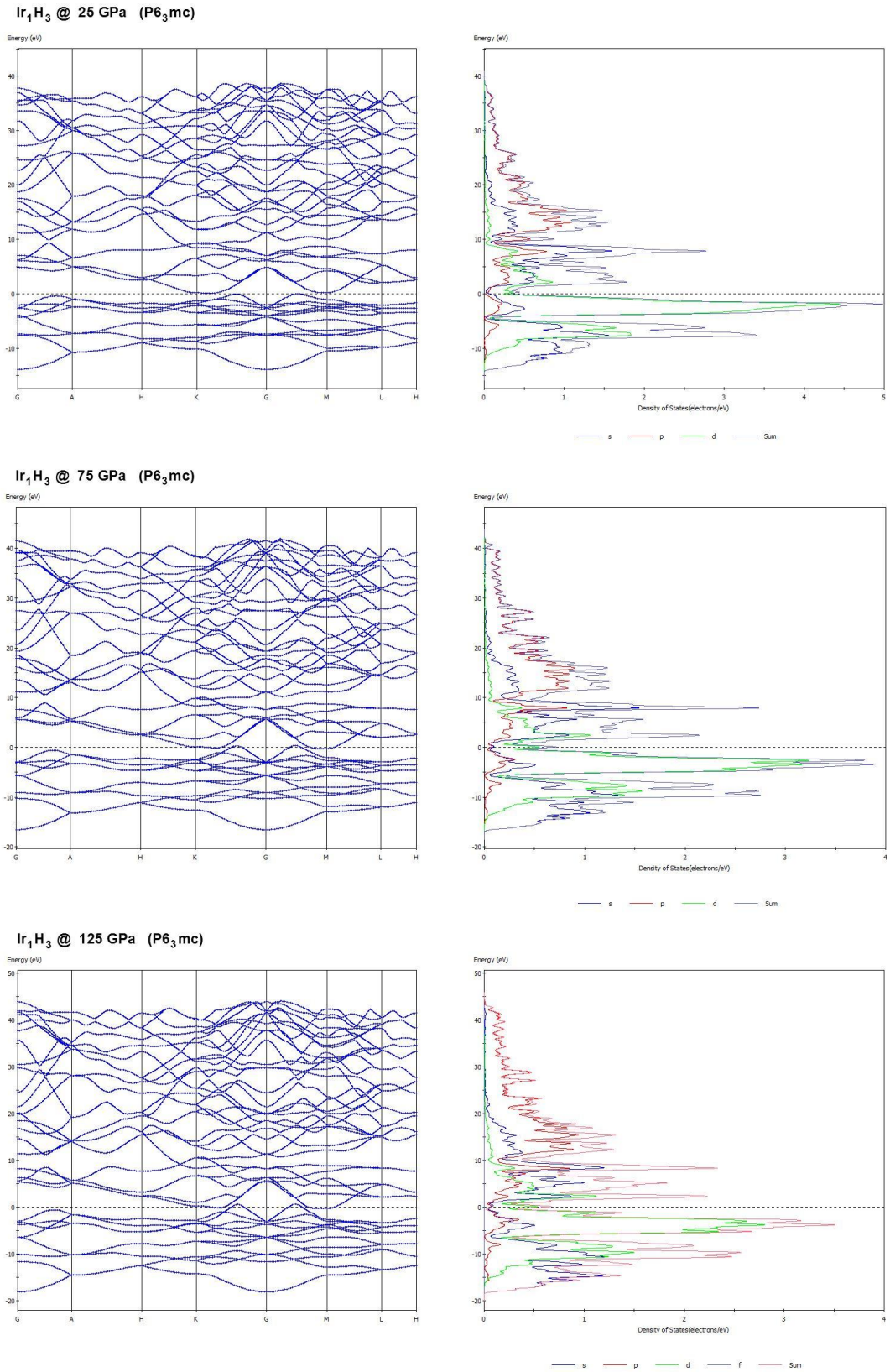

Fig. S8. Band structure and DOS calculated for IrH_3 ($P6_3mc$) at 25 (top), 75 (middle) and 125 GPa (bottom).

SELECTED STRUCTURES (.cif)

1. Ir_2H (R-3m, Z=2) @ 125 GPa

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#======================================================================

data_VESTA_phase_1

_pd_phase_name                         'Ir2H,\Z=2,\125GPa\(R-3m)              '
_cell_length_a                       4.53399
_cell_length_b                       4.53399
_cell_length_c                       4.53399
_cell_angle_alpha                    33.45726
_cell_angle_beta                     33.45726
_cell_angle_gamma                    33.45726
_symmetry_space_group_name_H-M       'P 1'
_symmetry_Int_Tables_number          1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  H1        1.0     0.000000     -0.000000     0.000000     Biso  1.000000 H
  Ir1       1.0     0.753071     0.753071     0.753071     Biso  1.000000 Ir
  Ir2       1.0     0.246929     0.246929     0.246929     Biso  1.000000 Ir

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2. IrH (Fm-3m, Z=1) @ 125 GPa

```
#======================================================================

data_VESTA_phase_1


_pd_phase_name                         'Ir1H1,\Z=1,\125GPa\()           '
_cell_length_a                       2.66946
_cell_length_b                       2.66946
_cell_length_c                       2.66946
_cell_angle_alpha                    60.00000
_cell_angle_beta                     60.00000
_cell_angle_gamma                    60.00000
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_B_iso_or_equiv
   _atom_site_type_symbol
   H1         1.0     0.500000      0.500000      0.500000     Biso  1.000000 H
   Ir1        1.0    -0.000000      0.000000     -0.000000     Biso  1.000000 Ir

#======================================================================
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3a. IrH_2 (Ibam, Z=2) @ 125 GPa

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#======================================================================

data_Ir1H2,\Z=2,\125GPa\(Ibam)

_symmetry_space_group_name_H-M    ' '
_symmetry_Int_Tables_number       0
_symmetry_cell_setting            orthorhombic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  y-z,x-z,-z
  -y+z+1/2,-y+1/2,x-y
  -x+1/2,-x+z+1/2,-x+y
  -x,-y,-z
  -y+z,-x+z,z
  y-z+1/2,y+1/2,-x+y
  x+1/2,x-z+1/2,x-y
_cell_length_a                  3.7246
_cell_length_b                  3.7246
_cell_length_c                  3.7246
_cell_angle_alpha                 105.7075
_cell_angle_beta                  139.0187
_cell_angle_gamma                  88.5302
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
H1     H    -0.21331   0.84108  -0.37223   0.01267  Uiso   1.00
Ir1    Ir   -0.25000   0.25000  -0.50000   0.01267  Uiso   1.00

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3b. IrH_2 (Cmcm, Z=4) @ 125 GPa

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#======================================================================

data_Ir1H2,\Z=4,\125GPa\(Cmcm)

_symmetry_space_group_name_H-M    ' '
_symmetry_Int_Tables_number       0
_symmetry_cell_setting            orthorhombic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,-y,z+1/2
  y,x,-z+1/2
  -y,-x,-z
  -x,-y,-z
  x,y,-z+1/2
  -y,-x,z+1/2
  y,x,z
_cell_length_a                    3.7046
_cell_length_b                    3.7046
_cell_length_c                    4.5263
_cell_angle_alpha                 90.0000
_cell_angle_beta                  90.0000
_cell_angle_gamma                 90.4084
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
H1     H     1.28127  -0.71873  -0.04841   0.01267  Uiso   1.00
H5     H     1.00000  -1.00000   0.00000   0.01267  Uiso   1.00
H6     H     0.40950  -0.59050  -0.75000   0.01267  Uiso   1.00
Ir1    Ir    0.63313  -0.87708  -0.25000   0.01267  Uiso   1.00

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4a. IrH_3 ($P6_3cm$, Z=2) @ 125 GPa

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#======================================================================

data_VESTA_phase_1

_pd_phase_name                         'Ir1H3,\Z=2,\150GPa\(P63mc)           '
_cell_length_a                       3.48469
_cell_length_b                       3.48469
_cell_length_c                       3.36142
_cell_angle_alpha                      90
_cell_angle_beta                       90
_cell_angle_gamma                        120.00213
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  H1        1.0     0.864194     0.728375     0.719671     Biso  1.000000 H
  H2        1.0     0.271624     0.135805     0.719671     Biso  1.000000 H
  H3        1.0     0.864192     0.135809     0.719657     Biso  1.000000 H
  H4        1.0     0.135806     0.271625     0.219671     Biso  1.000000 H
  H5        1.0     0.728375     0.864195     0.219671     Biso  1.000000 H
  H6        1.0     0.135808     0.864191     0.219658     Biso  1.000000 H
  Li1       1.0    0.333336     0.666664     0.849862     Biso  1.000000 Li
  Li2       1.0    0.666664     0.333336     0.349858     Biso  1.000000 Li

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4b. IrH_3 (Pm-3m, Z=2) @ 125 GPa

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#======================================================================

data_Ir1H3,\Z=1,\150GPa\(Pm-3m)

_audit_creation_date              2013-07-31
_symmetry_space_group_name_H-M    'PM-3M'
_symmetry_Int_Tables_number       221
_symmetry_cell_setting            cubic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  -x,-y,z
  -x,y,-z
  x,-y,-z
  z,x,y
  z,-x,-y
  -z,-x,y
  -z,x,-y
  y,z,x
  -y,z,-x
  y,-z,-x
  -y,-z,x
  y,x,-z
  -y,-x,-z
  y,-x,z
  -y,x,z
  x,z,-y
  -x,z,y
  -x,-z,-y
  x,-z,y
  z,y,-x
  z,-y,x
  -z,y,x
  -z,-y,-x
  -x,-y,-z
  x,y,-z
  x,-y,z
  -x,y,z
  -z,-x,-y
  -z,x,y
  z,x,-y
  z,-x,y
  -y,-z,-x
  y,-z,x
  -y,z,x
  y,z,-x
  -y,-x,z
  y,x,z
  -y,x,-z
```

```
  y,-x,-z
  -x,-z,y
  x,-z,-y
  x,z,y
  -x,z,-y
  -z,-y,x
  -z,y,-x
  z,-y,-x
  z,y,x
_cell_length_a                 2.5870
_cell_length_b                 2.5870
_cell_length_c                 2.5870
_cell_angle_alpha               90.0000
_cell_angle_beta                90.0000
_cell_angle_gamma                 90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
H1     H     0.50000   0.50000   0.00000   0.01267  Uiso   1.00
Ir1    Ir    1.00000  -0.00000   0.00000   0.01267  Uiso   1.00

#=============================================================================
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5. IrH_4 (I4/mmm, Z=2) @ 125 GPa

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#======================================================================

data_Ir1H4,\Z=2,\125GPa\(I4,mmm)

_symmetry_space_group_name_H-M    ' '
_symmetry_Int_Tables_number       0
_symmetry_cell_setting            tetragonal
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  y-z,x-z,-z
  y,y-z,-x+y
  x-z,x,x-y
  -y+z,-y,x-y
  -x,-x+z,-x+y
  -x+z,-y+z,z
  -y,-x,-z
  -x,-y,-z
  -y+z,-x+z,z
  -y,-y+z,x-y
  -x+z,-x,-x+y
  y-z,y,-x+y
  x,x-z,x-y
  x-z,y-z,-z
  y,x,z
_cell_length_a                  5.9808
_cell_length_b                  5.9808
_cell_length_c                  5.9808
_cell_angle_alpha               154.7714
_cell_angle_beta                154.7714
_cell_angle_gamma               35.9794
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
H1     H    -0.00000  -0.50000  -0.00000   0.01267  Uiso   1.00
H2     H     0.50000  -1.00000   0.50000   0.01267  Uiso   1.00
H3     H    -0.38110  -0.38110  -0.00000   0.01267  Uiso   1.00
Ir1    Ir    0.11482  -0.88518  -0.00000   0.01267  Uiso   1.00

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6. IrH_6 (P1, Z=2) @ 125 GPa

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#======================================================================

data_VESTA_phase_1

_pd_phase_name                         'EA  19  3.775  3.716  3.536 102.264 76'
_cell_length_a                       3.79227
_cell_length_b                       3.79230
_cell_length_c                       3.60439
_cell_angle_alpha                    102.72850
_cell_angle_beta                     77.26888
_cell_angle_gamma                    107.36810
_symmetry_space_group_name_H-M         'P 1'
_symmetry_Int_Tables_number            1

loop_
_symmetry_equiv_pos_as_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_B_iso_or_equiv
   _atom_site_type_symbol
   H1         1.0     0.037168     0.805582     0.045374     Biso  1.000000 H
   H2         1.0     0.998827     0.173516     0.321284     Biso  1.000000 H
   H3         1.0     0.185132     0.182415     0.903017     Biso  1.000000 H
   H4         1.0     0.176228     0.997307     0.483018     Biso  1.000000 H
   H5         1.0     0.808476     0.034572     0.760702     Biso  1.000000 H
   H6         1.0     0.924620     0.921745     0.902831     Biso  1.000000 H
   H7         1.0     0.634269     0.389671     0.149861     Biso  1.000000 H
   H8         1.0     0.697044     0.896271     0.188340     Biso  1.000000 H
   H9         1.0     0.941621     0.447052     0.889803     Biso  1.000000 H
   H10        1.0     0.449852     0.939156     0.916275     Biso  1.000000 H
   H11        1.0     0.899178     0.694503     0.617655     Biso  1.000000 H
   H12        1.0     0.392272     0.631850     0.656475     Biso  1.000000 H
   Ir1        1.0     0.604683     0.271287     0.584188     Biso  1.000000 Ir
   Ir2        1.0     0.273909     0.602207     0.222238     Biso  1.000000 Ir

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