Supporting Information

Disclosing the behavior under hydrostatic pressure of rhombohedral $MgIn_2Se_4$ by means of first-principles calculations

Khaled Boukri[a], Tarik Ouahrani [a,b,*] , Michael Badawi[c], Kamel Demmouche[d], Ruth Franco[e] and J. Manuel Recio[e,*]

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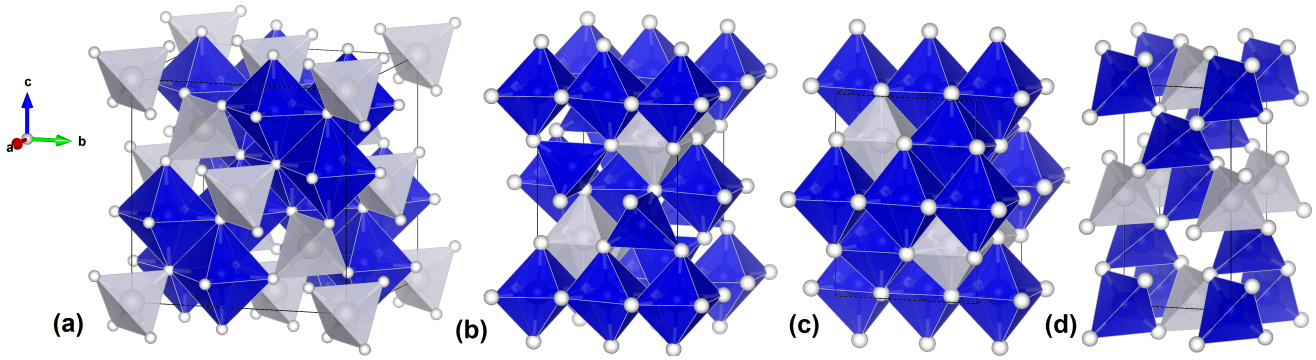

Fig. 1 Polyhedral views of (a) direct spinel, (b) inverse spinel, (c) $LiTiO_2$-type, and (d) $\bar{I}4$ polymorphs of $MgIn_2Se_4$.

[a] *Laboratoire de Physique Théorique, Université de Tlemcen 13000 Algeria. Tel:+21343201824; E-mail: tarik_ouahrani@yahoo.fr*

[b] *École supérieure en sciences appliquées, B.P. 165, Tlemcen 13000, Algeria.*

[c] *Université de Lorraine and CNRS, LPCT, UMR 7019, 54506 Vandoeuvre-lés-Nancy, France*

[d] *Institut des Sciences, Centre Universitaire -Belhadj Bouchaib- Ain Temouchent, B.P. 284, 46000 Ain Temouchent, Algeria*

[e] *MALTA-Consolider Team and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33006 Oviedo Spain*

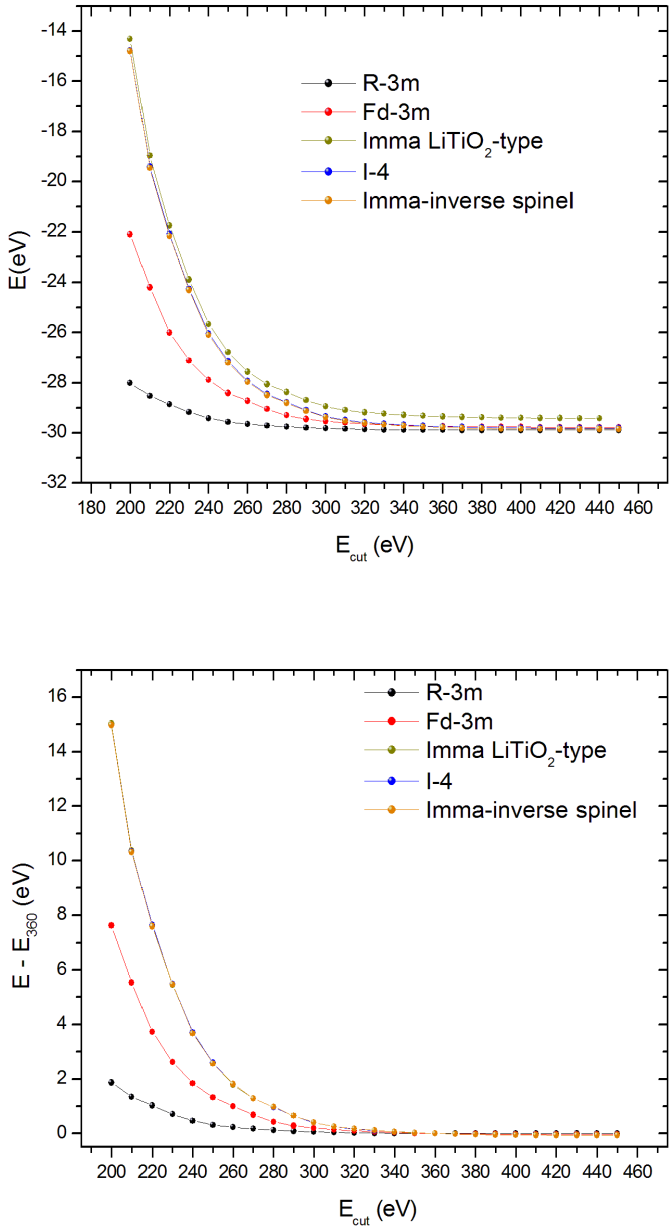

Fig. 2 Test of energy convergence with the plane wave kinetic energy cutoff (E_{cut}). (Top) Total energy (E) and (bottom) relative total energy ($E - E_{360}$) *versus* E_{cut} for the five $MgIn_2Se_4$ polymorphs explored in this work. E_{360} is the energy when E_{cut} = 360 eV for each polymorph.

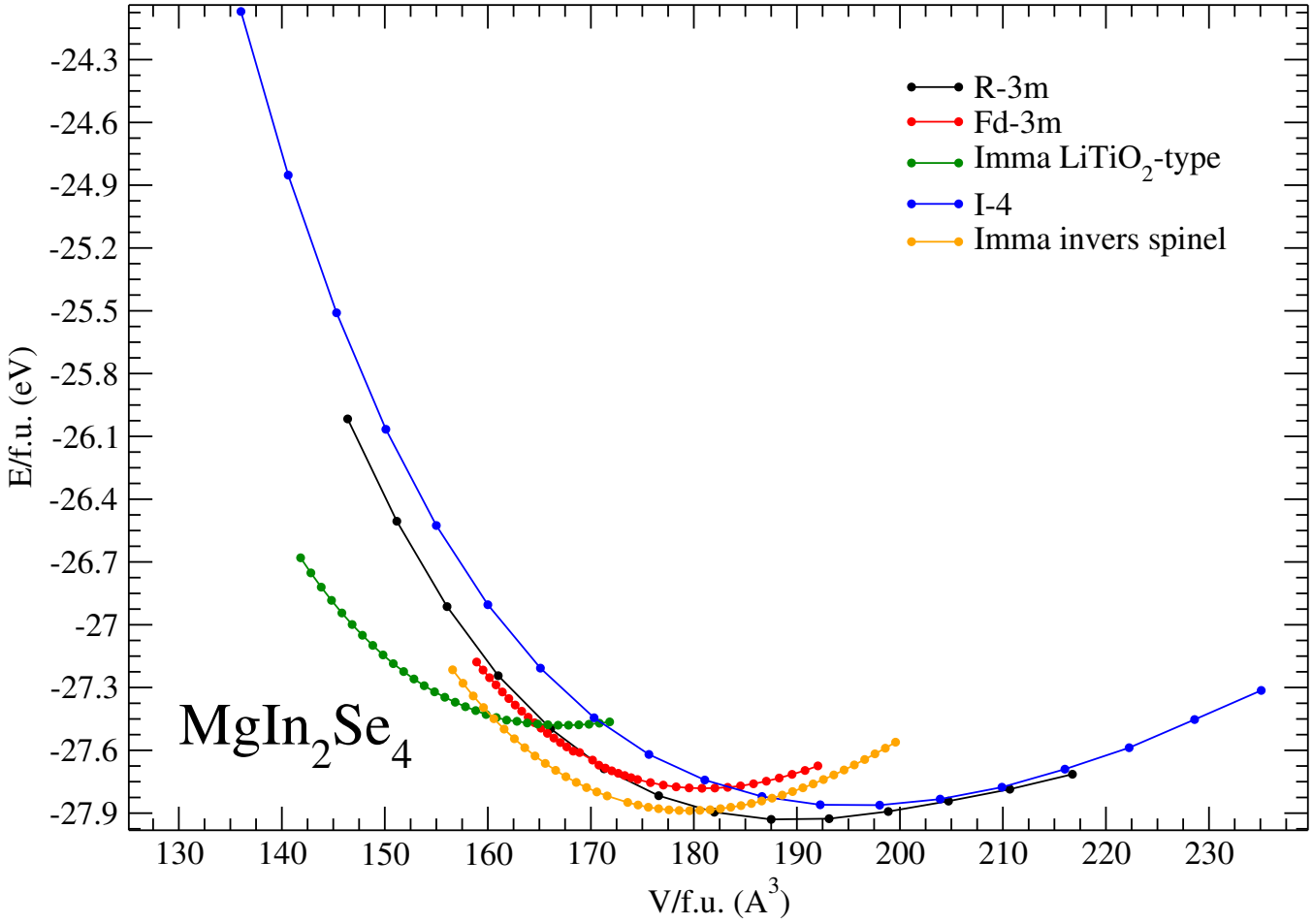

Fig. 3 Volume dependence of the electronic energy of $MgIn_2Se_4$ according to GGA-PBE+D3 calculations for the $R\bar{3}m$(a), *Imma* inverse spinel(b), $Fd\bar{3}m$(c), *Imma* $LiTiO_2$-type(d), and $I\bar{4}$(e), structures. Symbols stand for the calculated values, whereas lines are a guide to the eye. All values for formula unit.

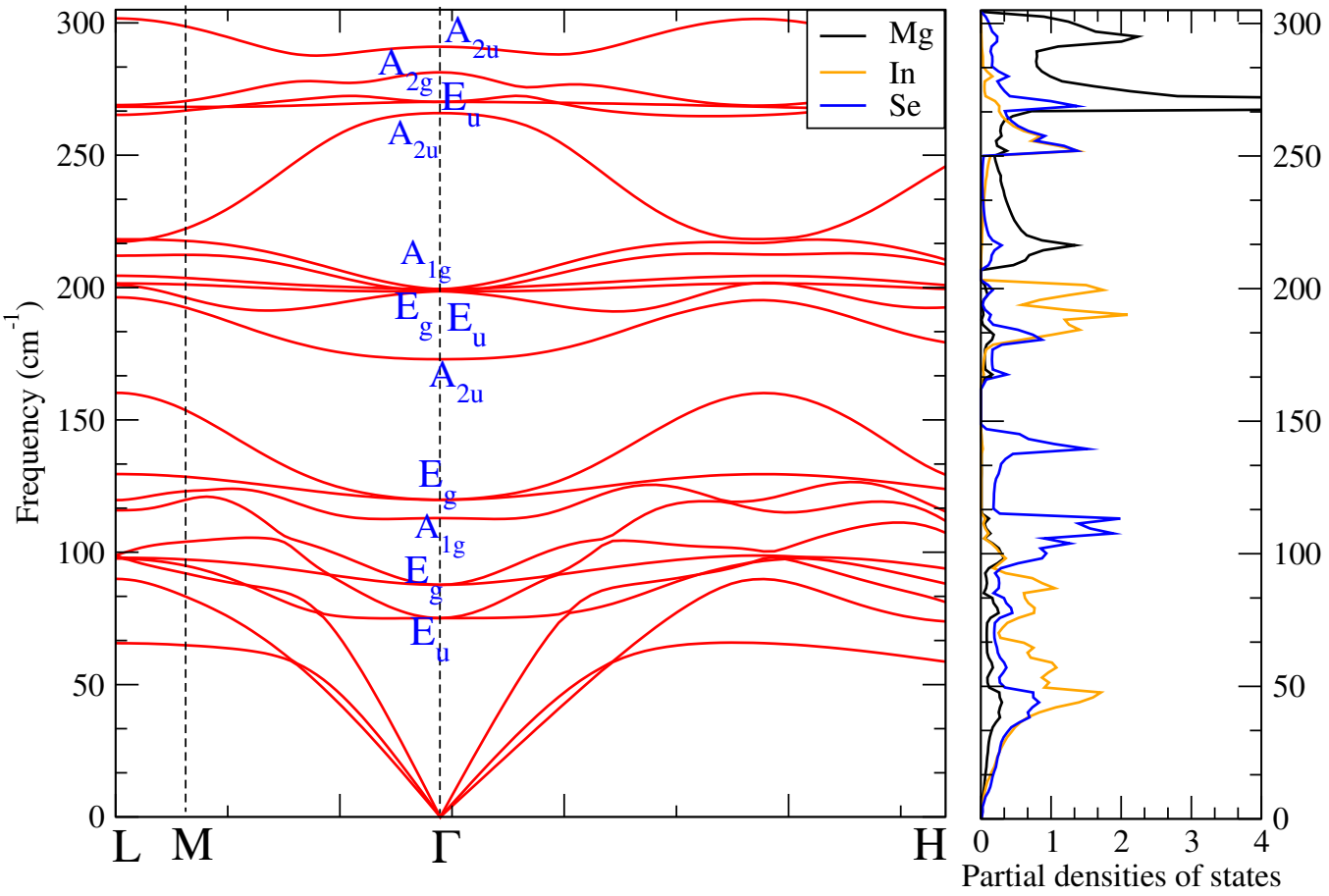

Fig. 4 Phonon dispersion curves calculated at GGA-PBE+D3 level for the $R\bar{3}m$ phase at zero pressure.

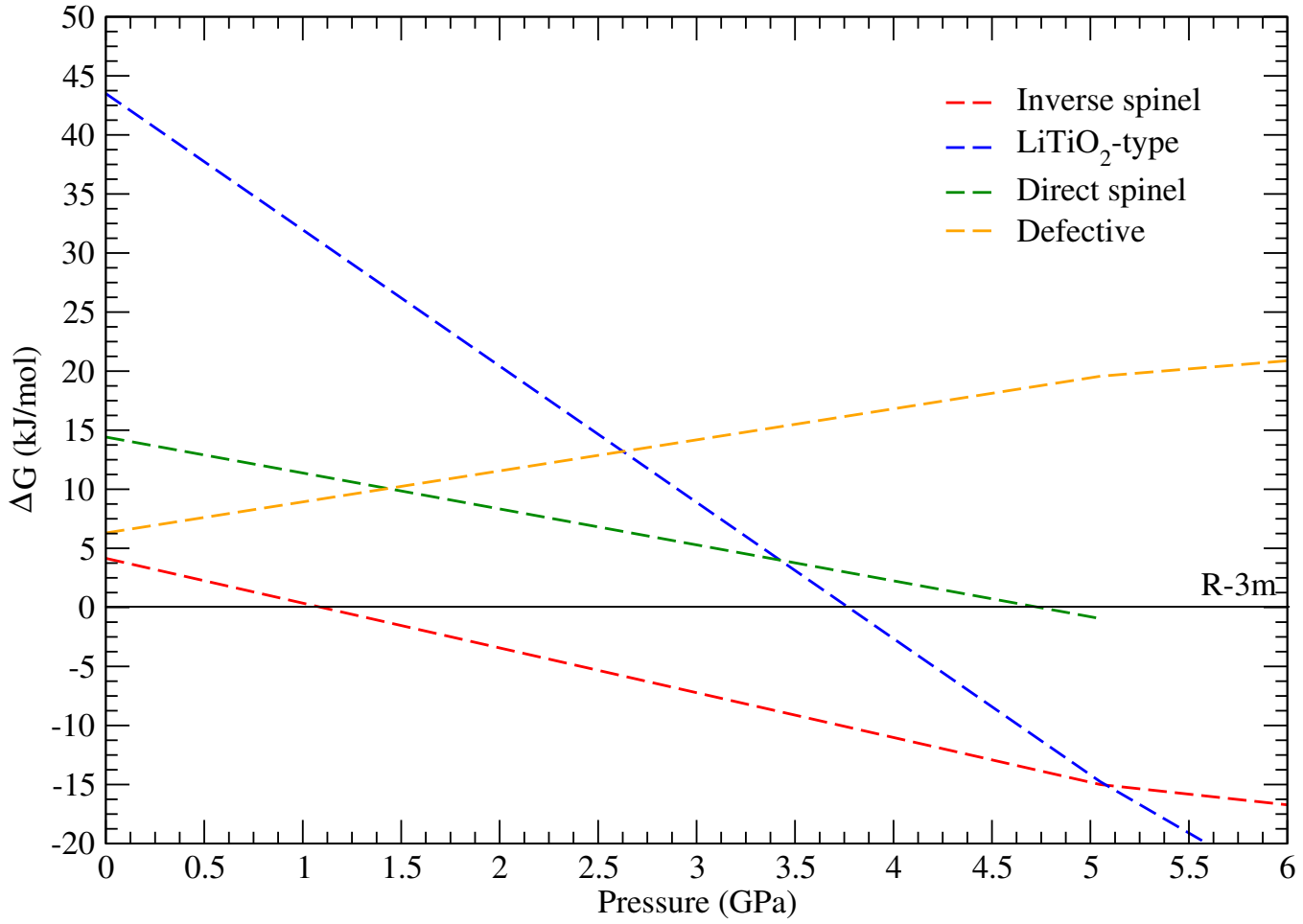

Fig. 5 Pressure dependence of the Gibbs energy at GGA-PBE+D3 level at static conditions.

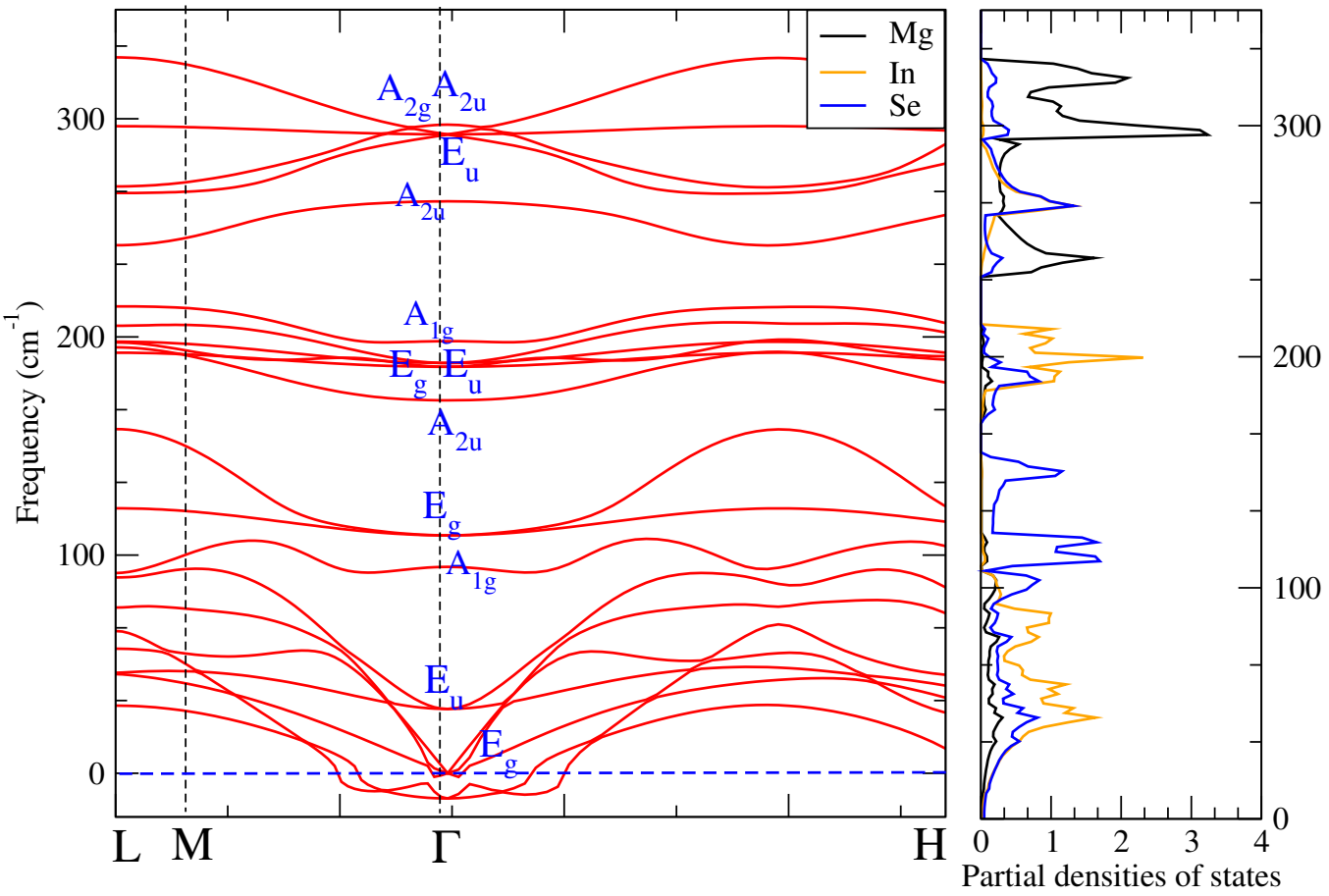

Fig. 6 Phonon dispersion curves calculated at GGA-PBE+D3 level for the $R\bar{3}m$ phase at 1.5 GPa.

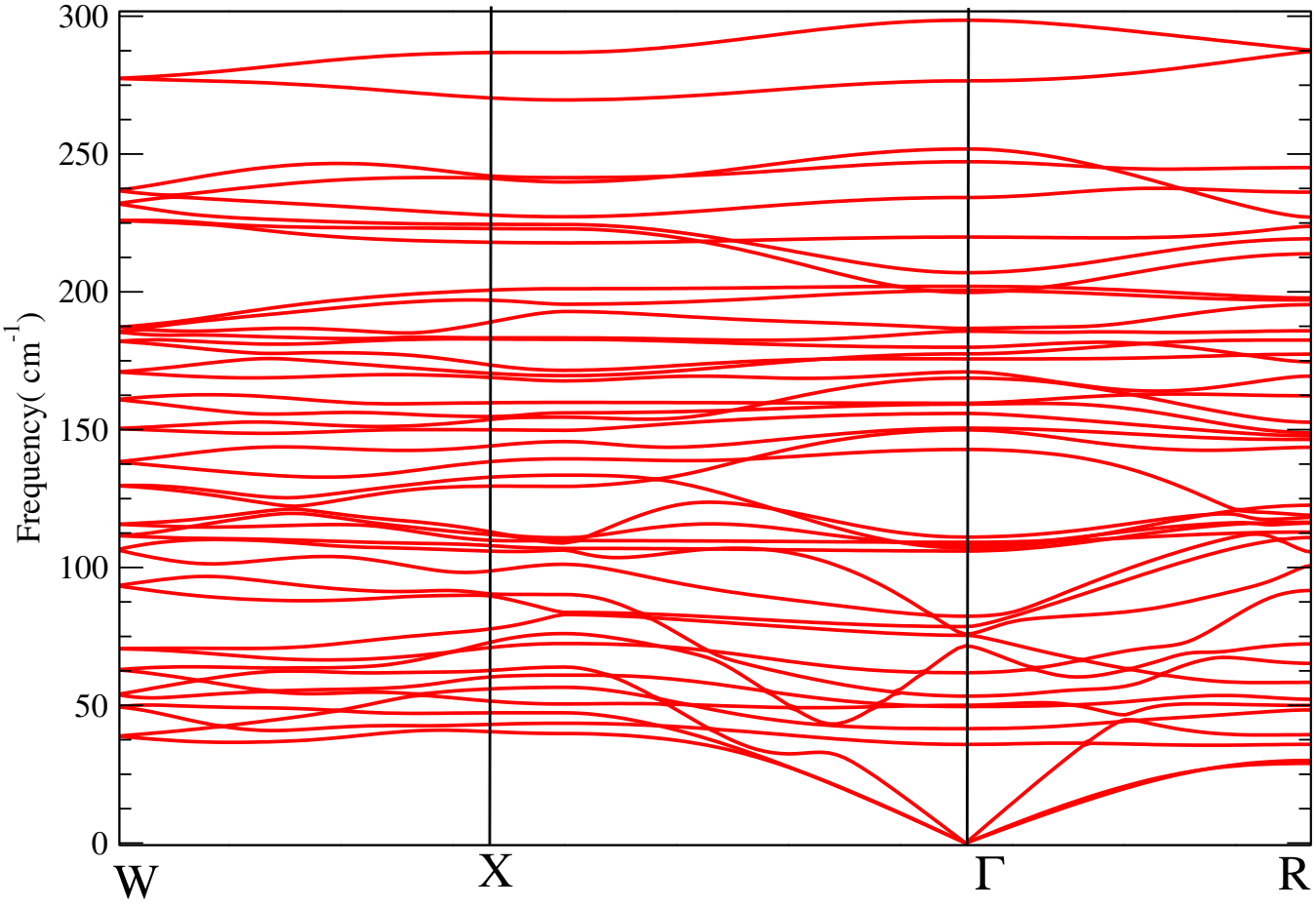

Fig. 7 Phonon dispersion curves calculated at GGA-PBE+D3 level for the inverse spinel phase at 2.5 GPa.

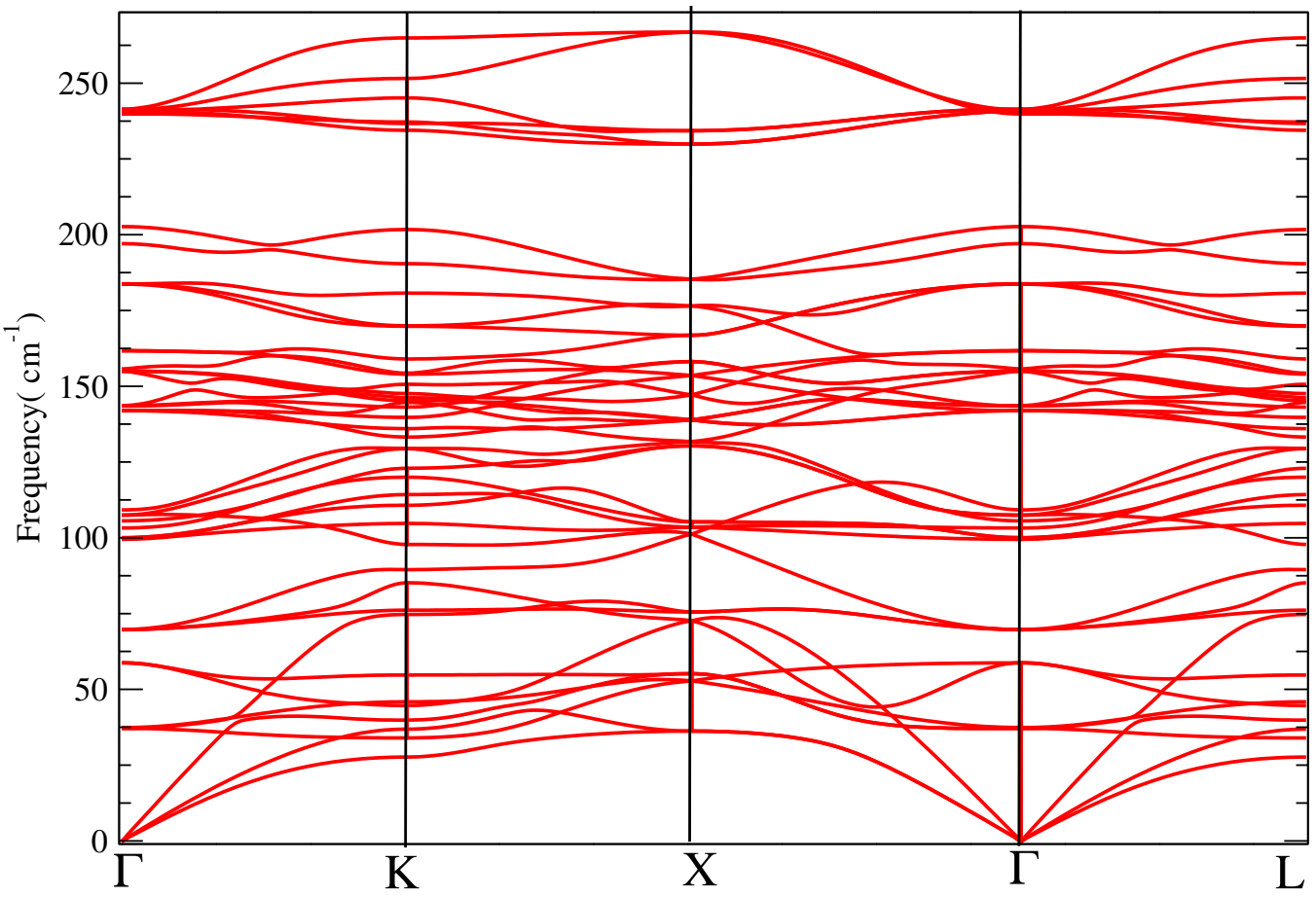

Fig. 8 Phonon dispersion curves calculated at GGA-PBE+D3 level for the direct spinel phase at 5 GPa.

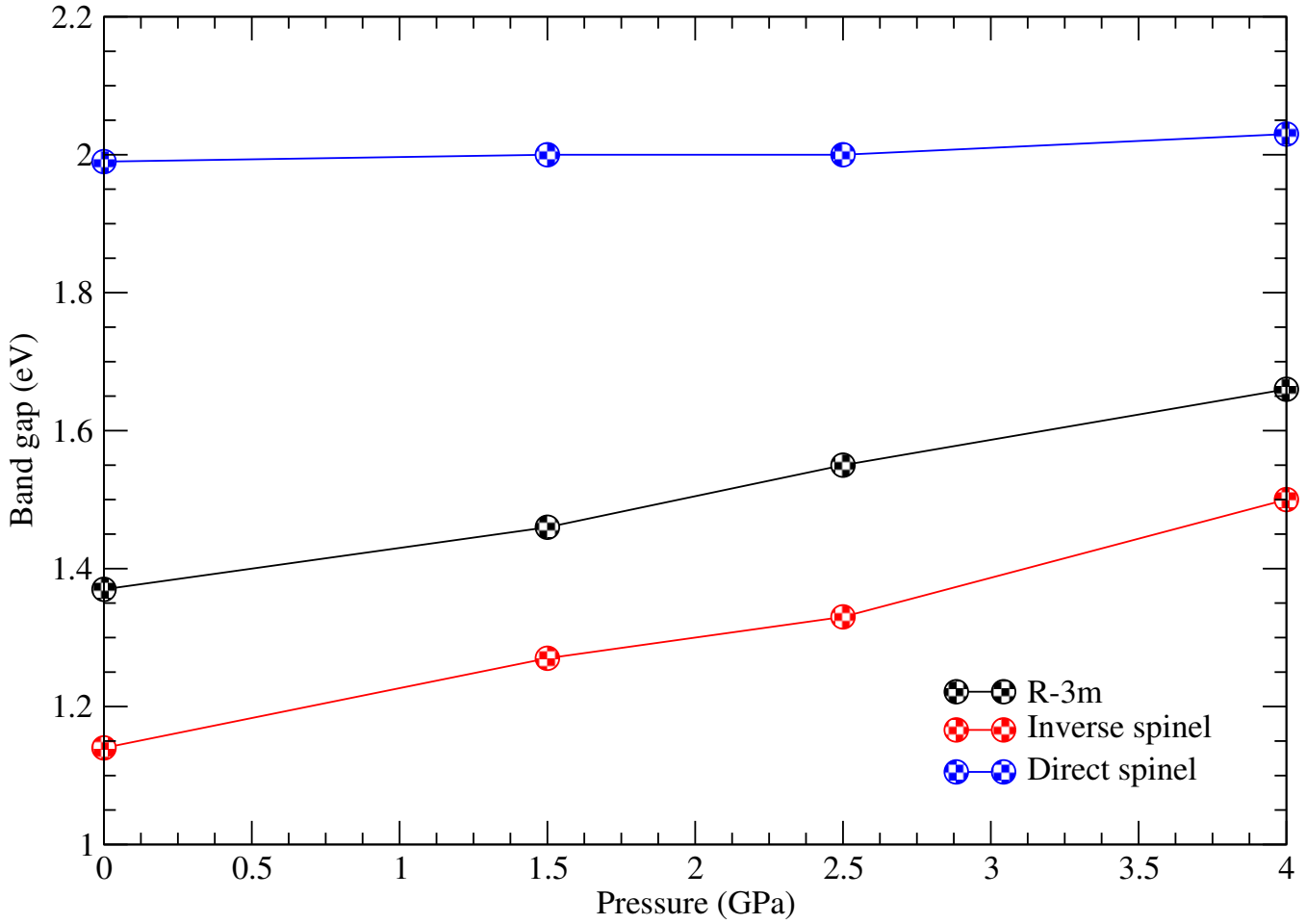

Fig. 9 Pressure evolution of the band gap of the $R\bar{3}m$, Inverse and direct spinel polymorphs according to our calculations using the hybrid HSE06 functional.

Table 1 Crystallographic coordinates of atoms in the five polymorphs of $MgIn_2Se_4$ explored in this work. The space group, symmetry multiplicity, and the number of formula units (Z) are given.

Atom	Wyckoff position	x	y	z
Rhombohedral ($R\bar{3}m$), Z = 3				
LDA+D3				
In1	6c	0.00000	0.00000	0.23524
Se1	6c	0.00000	0.00000	0.12966
Se2	6c	0.00000	0.00000	0.29935
GGA-PBE+D3				
In1	6c	0.00000	0.00000	0.23709
Se1	6c	0.00000	0.00000	0.12673
Se2	6c	0.00000	0.00000	0.30002
Inverse spinel (*Imma*), Z = 4				
LDA+D3				
In2	4e	0.00000	0.25000	0.13398
Se1	8h	0.00000	0.02542	0.74334
Se2	8i	0.23719	0.25000	0.50907
GGA-PBE+D3				
In2	4e	0.00000	0.25000	0.13362
Se1	8h	0.00000	0.02518	0.74339
Se2	8i	0.23721	0.25000	0.50946
Direct spinel ($Fd\bar{3}m$), Z = 8				
LDA+D3				
Se1	32e	0.75692	0.75692	0.75692
GGA-PBE+D3				
Se1	32e	0.75654	0.75654	0.75654
$LiTiO_2$-type (*Imma*), Z = 4				
LDA+D3				
Se1	8h	0.00000	-0.00783	0.74285
Se2	8i	0.25354	0.25000	0.50167
GGA-PBE+D3				
Se1	8h	0.00000	-0.00642	0.74352
Se2	8i	0.25326	0.25000	0.50175
Defective ($I\bar{4}$), Z = 2				
LDA+D3				
Se	1 8g	0.21618	0.72006	0.36085
GGA-PBE+D3				
Se1	8g	0.21593	0.72217	0.36193