Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Framework Reconstruction between *hR*8 and *cI*16 Germaniums: A Molecular Dynamics Study

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Intermediate *hR*32 Structure

The intermediate appearing along the reaction coordinate of the *hR*8←→*cI*16 network reconstruction corresponds to a novel structural motif, which is isosymmetric with *hR*8. Structural (Table S1) and cell parameters (sp. gr. $R\bar{3}$, *a*= 117.058 pm, α= 117.02°) were optimized with SIESTA (Table 1).[1] A double-ζ basis and the PBE form of the GGA functional were used. Core states were described by norm-conserving Troullier-Martins pseudopotentials.[2] Convergence of the total energy with respect to number of k points was carefully checked.

Table S1: Structural parameters for *hR*32.

Atom	Multiplicity	X	Y	Z
Ge1	6	0.73075	0.13191	0.38248
Ge2	6	0.74004	0.64066	0.89041
Ge3	6	0.23572	0.13597	0.88540
Ge4	6	0.23774	0.63638	0.38723
Ge5	6	0.78941	0.28964	0.28996
Ge6	2	0.70296	0.70296	0.70296

Phonon dispersion curves (Figure S1) were calculated at 0 GPa. No imaginary frequencies were observed throughout the whole Brillouin zone, confirming the dynamical stability of the intermediate *hR*32 structure. Band structure calculations (DFTB+)[3] indicate that *hR*32 is a semiconductor (Figure S2).

(1) J. M. Soler, E. Artacho, J. D. Gale, A. Garca, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys. Condens. Matter 14, 2745 (2002).

(2) N. Troullier and J. L. Martins, Phys. Rev B 43, 1993 (1991).

(3) http://www.dftb-plus.info/.

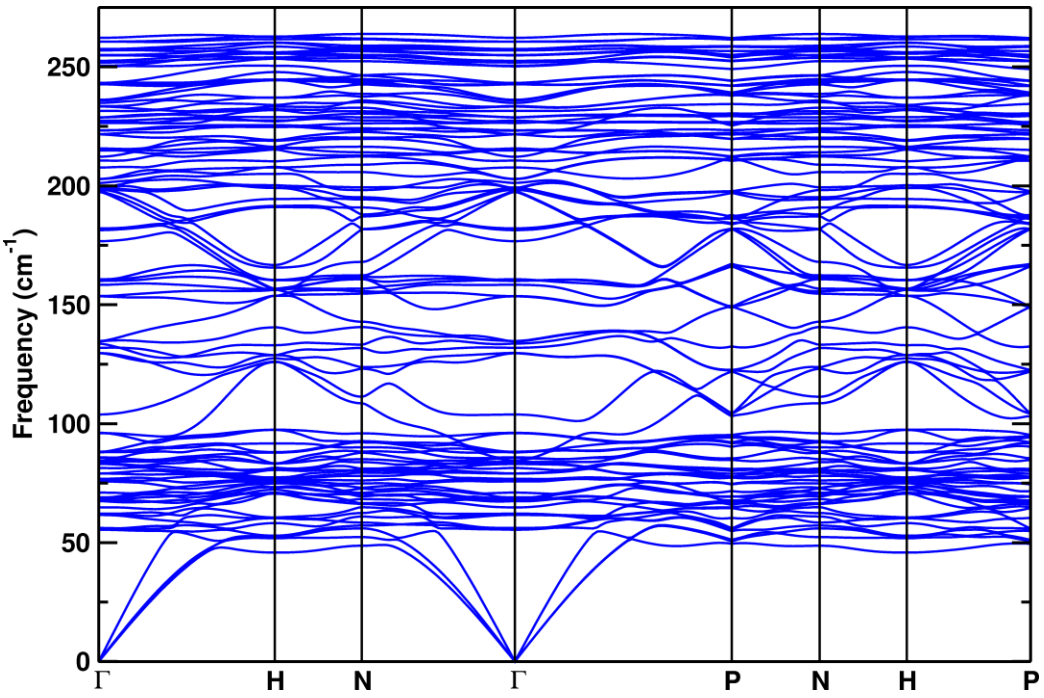

Figure S1: Phonon dispersion curves for *hR*32.

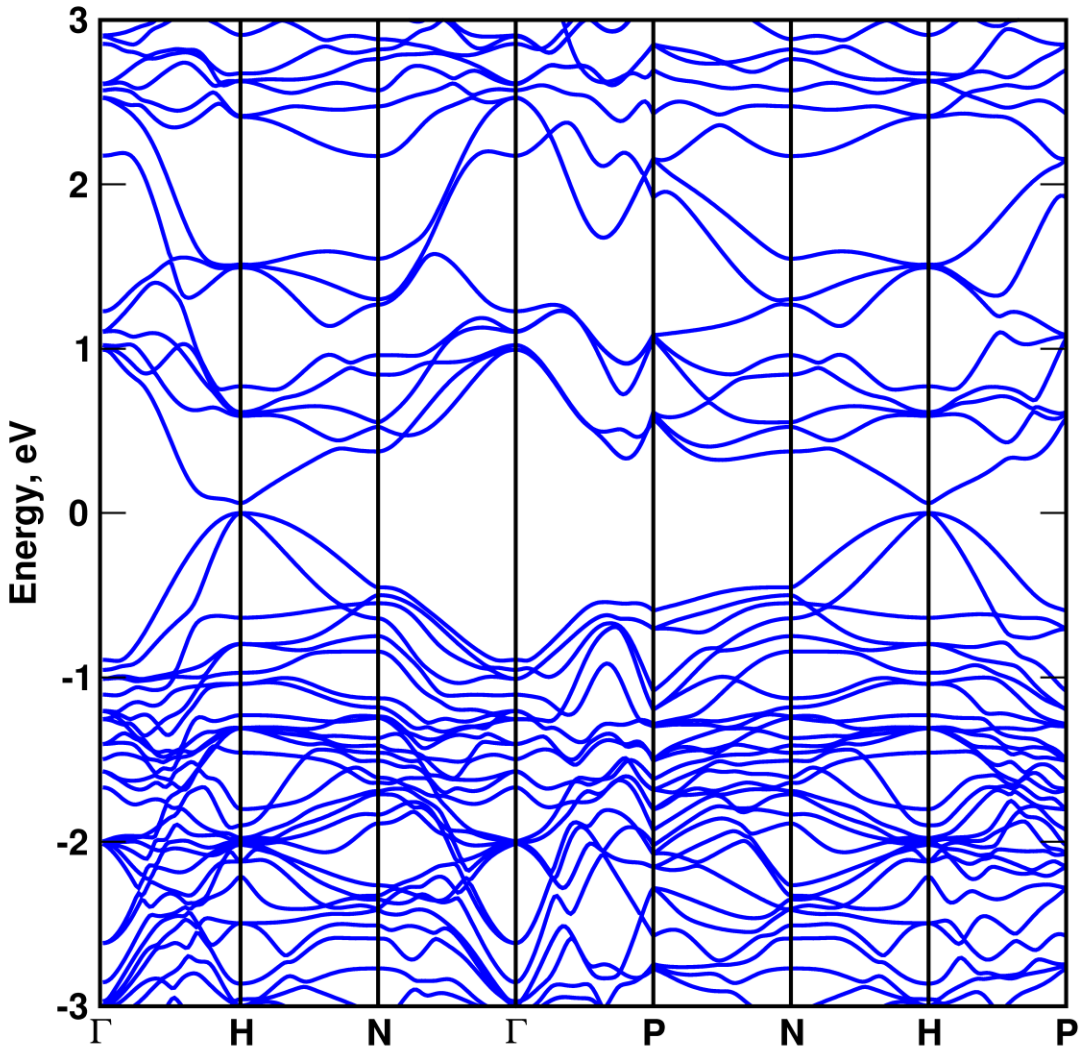

Figure S2: Band structure for *hR*32.

Table S2: Energetics of Ge Structures

	DFTB [eV/atom]	Volume [Å^3/atom]		DFT [eV/atom]	Volume [Å^3/atom]
		DFTB	Exp.	FPLO[7-9]	
cF8	0.00	25.86	22.56[4]	0.00	22.54
cI16	0.1489	23.83	20.81[5]	0.126	20.98
hR8	0.1758	23.58	20.30[6]	0.138	20.36

(4) Qadri, S.B.; Skelton, E.F.; Webb, A.W. *J. Appl. Phys.* **1983**, *54*, 3609

(5) Nelmes, R.J.; McMahon, M.I.; Wright, N.G.; Allan, D.R.; Loveday, J.S. *Phys. Rev. B* **1993,** *48*, 9883.

(6) Schwarz, U.; Wosylus, A.; Boehme, B.; Baitinger, M.; Hanfland, M.; Grin, Yu. Angew. Chem. Int. Ed. Engl. **2008**, *47,* 6790.

(7) FPLO-7, full-potential local-orbital minimum-basis code. Koepernik K.; Eschrig H. *Phys. Rev.* 1999, *59*, 1743.

(8) Perdew, P.; Wang, Y. *Phys. Rev.* **1992**, *45*, 13244.

(9) k-mesh (all structures): 12x12x12

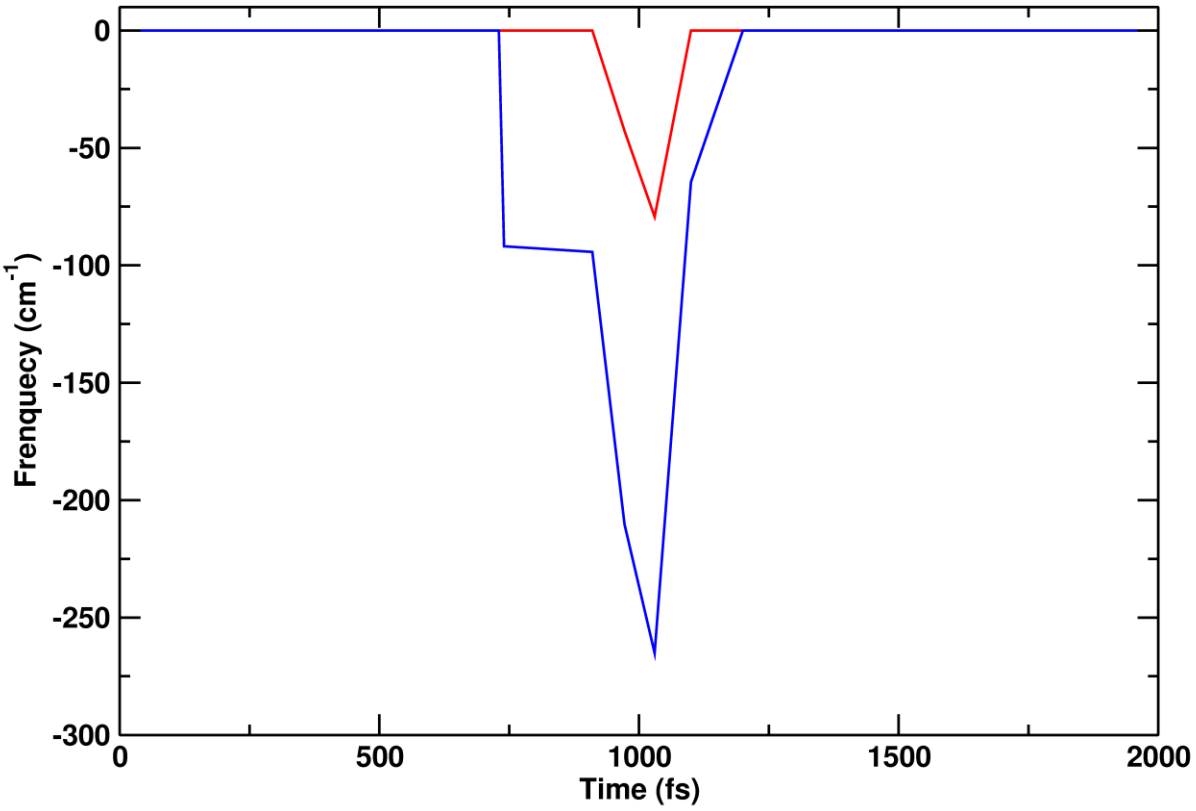

Figure S3: Evolution of phonon frequencies. “Blue” and “red” modi coexist in the intermediate region.