

# Supporting Information

Li et al. 10.1073/pnas.1307384110

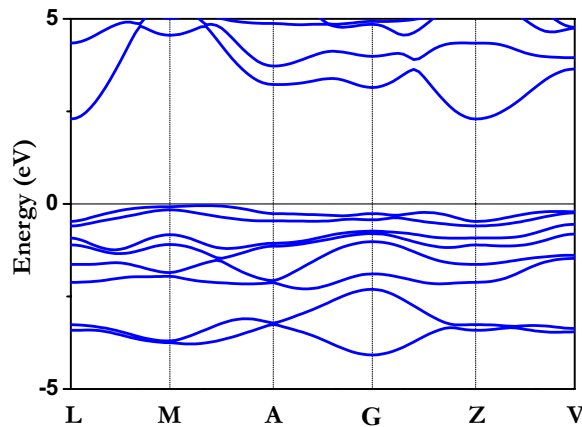


Fig. S1. Energy band of phase I at zero pressure using Perdew, Burke, and Ernzerhof exchange-correlation function and projected augmented wave pseudopotential as implemented in Vienna ab initio simulation package (1–4).

1. Kresse G, Furthmüller J (1996) Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput Mater Sci* 6(1):15–50.
2. Blöchl PE (1994) Projector augmented-wave method. *Phys Rev B Condens Matter* 50(24):17953–17979.
3. Kresse G, Joubert J (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B* 59(3):1758–1775.
4. Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. *Phys Rev Lett* 77(18):3865–3868.

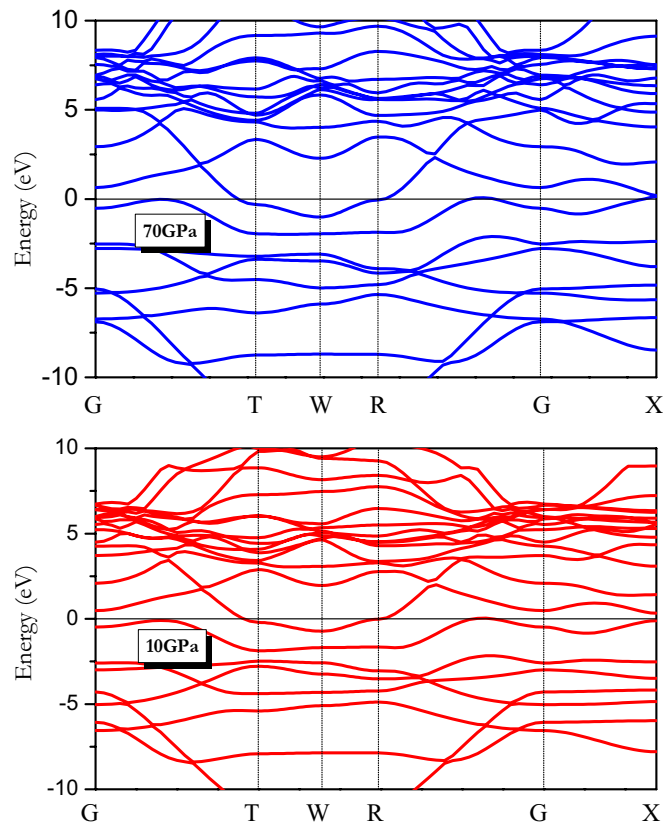


Fig. S2. Band structure of phase III at different pressure. Red line, 10 GPa; blue line, 70 GPa. Under compression, conduction band shifts to higher energy level, whereas covalence band shifts to lower level.

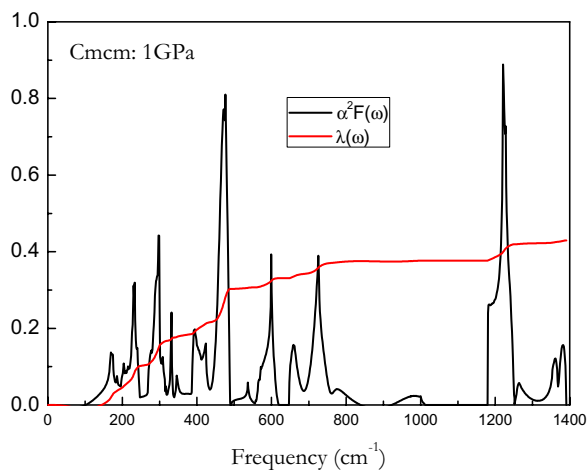


Fig. S3. The Eliashberg phonon spectral function  $\alpha^2 F(\omega)$  (black line) and integrated  $\lambda(\omega)$  (red line) for phase II at 1 GPa calculated using density functional perturbation theory as implemented in Quantum Espresso (1).

1. Giannozzi P, et al. (2009) QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J Phys Condens Matter* 21(39):395502.

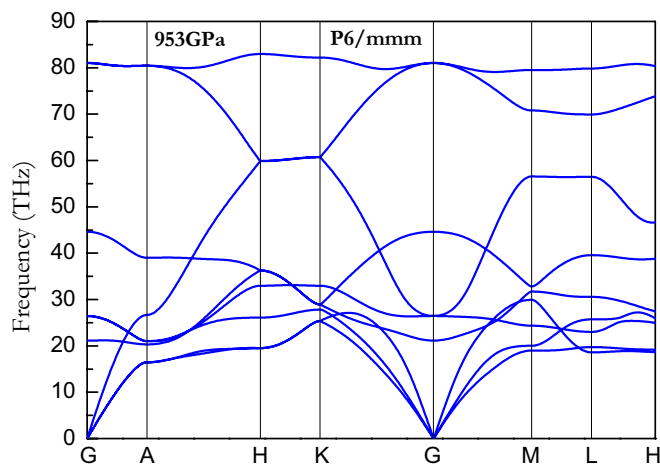


Fig. S4. Phonon spectrum of phase IV at 953 GPa from small displacement method via Phonopy code (1).

1. Togo A, Obe F, Tanaka I (2008) Ab initio up to the melting point: Anharmonicity and vacancies in aluminum. *Phys Rev B* 79(13):134106.

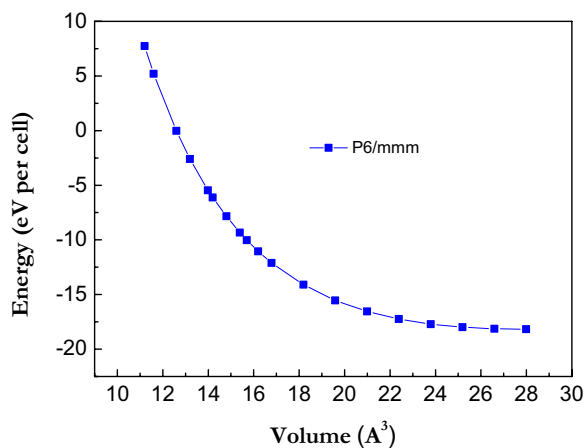
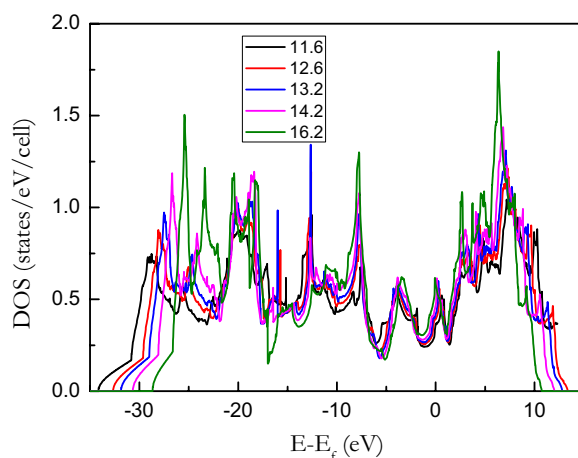


Fig. S5. Equation of state of phase IV.



**Fig. S6.** Electronic density of states (DOS) of phase IV at different volumes (in cubic angstroms) (200 GPa to 1 TPa). As pressure increases, DOS value at Fermi level ( $E_f$ ) decreases.

**Table S1. Structures of the stable phases of  $\text{CaC}_2$**

Pressure, GPa	Space group (no.)	Lattice parameters, $a, b, c, \alpha, \beta, \gamma; \text{\AA}, ^\circ$			Atomic fractional coordinates			
0	$C2/m$ (12)	7.1712	3.8463	8.7162	Ca 4i	0.0425	0.0000	0.2470
		90	124.99	90	C1 4i	0.6063	0.0000	0.0594
					C2 4i	0.5142	0.0000	0.4352
4	$Cmcm$ (63)	3.6822	8.6324	4.7360	Ca 4c	0.0000	0.1465	0.2500
15.2	$Immm$ (71)	7.0623	2.6317	6.2697	C 8f	0.000	0.4376	0.1028
		90	90	90	Ca 4e	0.2951	0.0000	0.0000
					C1 4i	0.0000	0.0000	0.2371
105.8	$P6/mmm$ (191)	2.5412	2.5412	3.6864	C2 4j	0.5000	0.0000	0.3829
		90	90	120	Ca 1a	0.0000	0.0000	0.0000
					C 2d	0.3333	0.6667	0.5000

Only the fractional coordinates of symmetry inequivalent atoms are given.

**Table S2. Atomic Mulliken population analysis for phase IV at 105.8 GPa obtained using CASTEP code (1)**

Atom	s	p	d	Total	Charge
C	1.11	3.29	—	4.39	-0.39
C	1.11	3.29	—	4.39	-0.39
Ca	1.80	5.92	1.49	9.22	0.78

1. Clark SJ, et al. (2005) First principles methods using CASTEP. *Z Kristallogr* 220(5-6):567-570.