SUPPORTING INFORMATION

Zintl ions within framework channels: the complex structure and low-temperature transport properties of Na_4Ge_{13}

Stevce Stefanoski[1], Gregory J. Finkelstein[2], Matthew D. Ward[1], Tao Zeng[3], Kaya Wei[4], Emma S. Bullock[1], Christine M. Beavers[5], Hanyu Liu[1], George S. Nolas[4], Timothy A. Strobel[1,*]

[1]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*
[2]*Seismological Laboratory, California Institute of Technology, Pasadena, CA 91125, USA*
[3]*Department of Chemistry, Carleton University, Ottawa, ON K1S5B6, Canada*
[4]*Department of Physics, University of South Florida, Tampa, FL, 33620, USA*
[5]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

Section S1. Interatomic Distances in the Na_4Ge_{13} crystal

Table S1. Selected Interatomic Distances for $Na_4Ge_{12}(Ge_4)_{0.25}$

Interaction/Distance (Å)									
Ge1		Ge3		Ge5		Na1a		Na1b	
−Ge1*	0.733(7)	−Ge2	2.494(1)	−Ge3 x2	2.497(1)	−Ge1*	2.754(5)	−Na1b*	0.496(12)
−Ge1 x2*	1.474(2)	−Ge5 x2	2.497(1)	−Ge4	2.512(1)	−Ge3 x2	3.223(3)	−Ge1*	2.261(7)
−Ge1 x2*	1.647(4)	−Na1b x2	3.178(5)	−Ge4	2.537(1)	−Ge3 x2	3.236(3)	−Ge1*	2.766(7)
−Ge6*	1.975(4)	−Na1b x2	3.210(5)	−Na2 x2	3.221(1)	−Ge1 x2	3.238(4)	−Ge1	3.134(6)
−Na1b*	2.261(7)	−Na1a x2	3.223(3)	−Na1a	3.305(4)	−Ge5	3.305(4)	−Ge1	3.159(6)
−Ge6	2.415(4)	−Na1a x2	3.236(3)			−Ge2	3.461(4)	−Ge1	3.171(6)
−Ge6	2.523(4)	−Na1b x2	3.474(6)					−Ge3	3.178(5)
−Ge1 x2	2.553(4)							−Ge3	3.210(5)
−Na1b*	2.590(6)							−Na1b x2*	3.275(5)
								−Ge6	3.276(6)
Ge2		Ge4		Ge6		Na2			
−Ge4 x2	2.460(1)	−Ge2 x2	2.460(1)	−Ge6*	0.599(8)	−Ge4 x6	3.196(1)		
−Ge2	2.464(1)	−Ge5	2.512(1)	−Ge1 x6*	1.975(4)	−Ge5 x6	3.221(1)		
−Ge3	2.494(1)	−Ge5	2.537(1)	−Ge1 x6	2.415(4)				
−Na1a	3.461(1)	−Na2 x2	3.196(1)	−Ge1 x6	2.523(4)				
		−Na1a	3.239(4)						

*These distances appear in the cif file for the fully occupied channel, but are not statistically possible based upon the proposed disorder. For Ge1, only one of the two possible interactions

with Ge6 will occur at any given site. For Ge6, only three of the possible twelve interactions with Ge1 will occur at any given site.

Section S2. Molecular orbital and bonding analysis

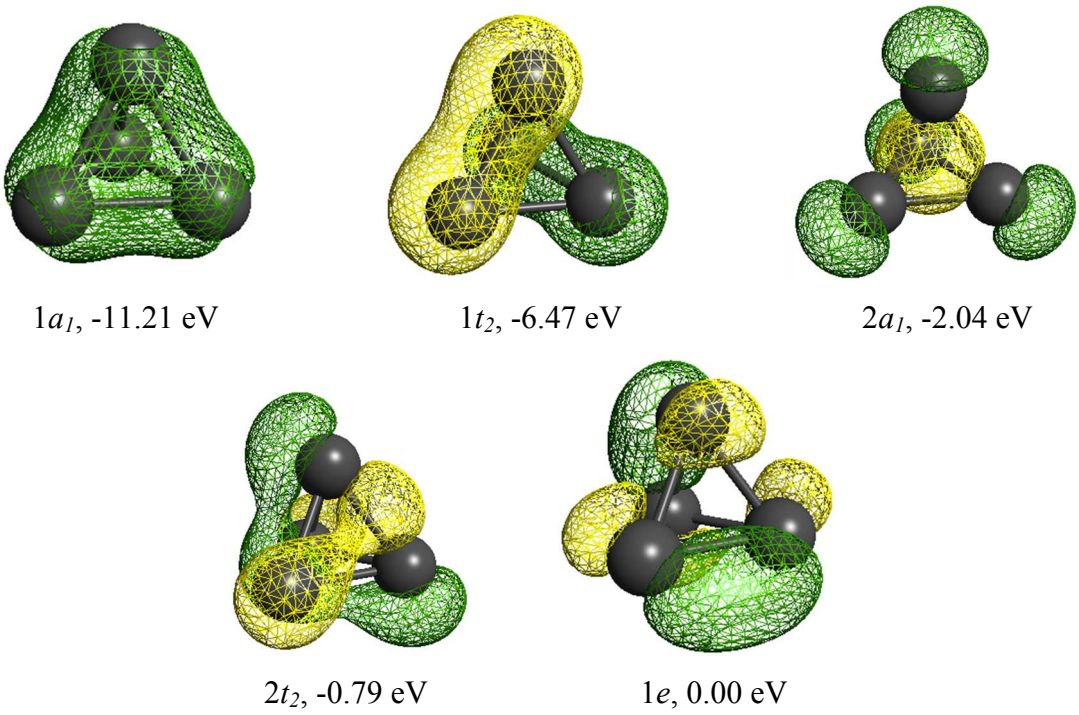
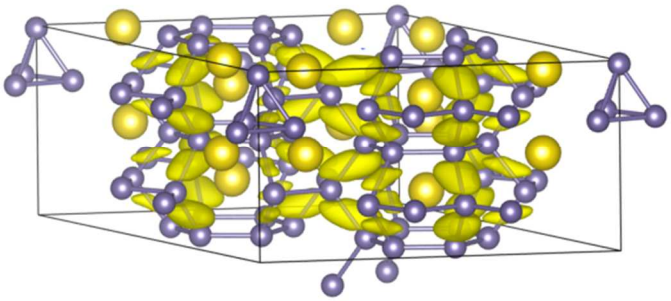
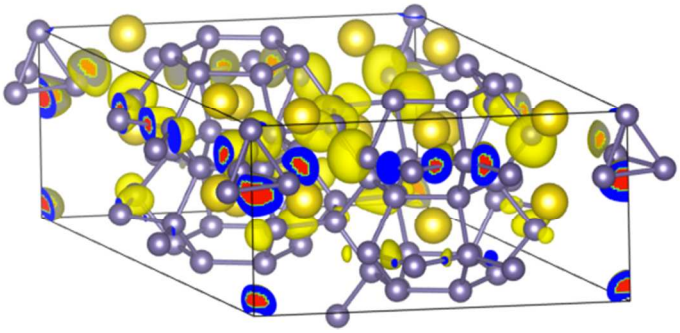


Figure S1. Valence occupied molecular orbitals of $[Ge_4]^{4-}$. Their energies are measured with respect to the highest occupied 1e orbitals.

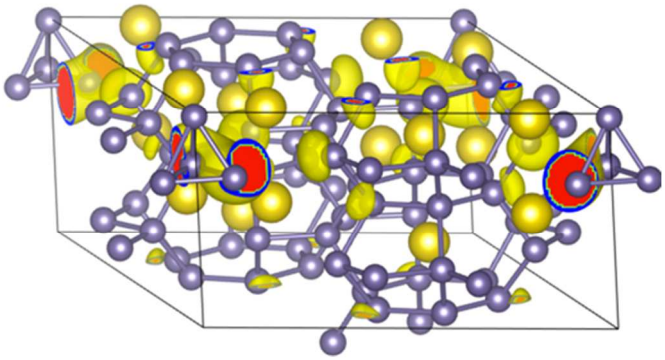
A few highest occupied crystal orbitals of the c×2 structure at the Γ point have their densities shown in Figure S2. In the second and third highest occupied crystal orbitals (HOCO), HOCO-1 and HOCO-2, we can see some contributions from the tetrahedra. They do not exactly look like the 1e and 2t_2 orbitals. However, with a slight distortion of the T_d structure, the two orbitals mix and contribute to the extended orbitals.



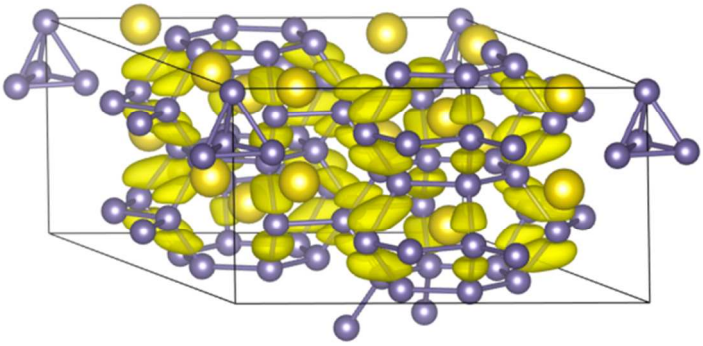
HOCO – 3 (2-fold degenerate)



HOCO – 2



HOCO – 1 (2-fold degenerate)



HOCO

Figure S2. Densities of the three highest occupied orbitals (HOCO) of c×2 at the Γ point.

d-Ge is a poor conductor with the conduction and valence bands touching with DOS = 0 (Figure S3). The ionic interaction with the Na^+ and the 3c Ge^- opens the band gap slightly to 0.16 eV and stabilizes the c×2 structure.

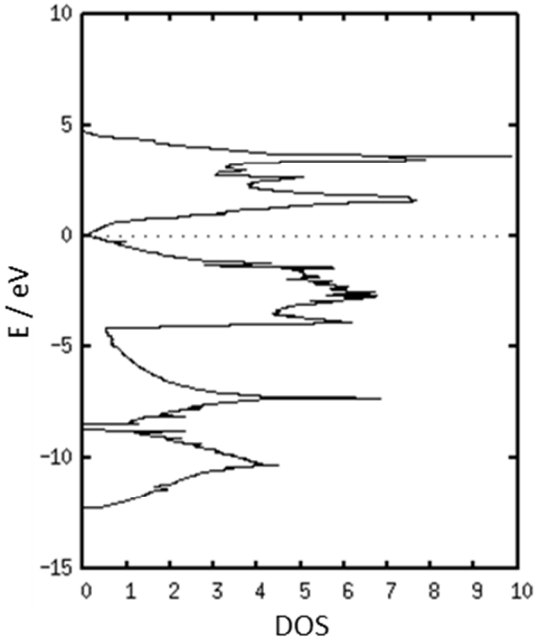


Figure S3. DOS of *d*-Ge. Fermi level is set to be 0 eV.

Staggered versus eclipsed configurations

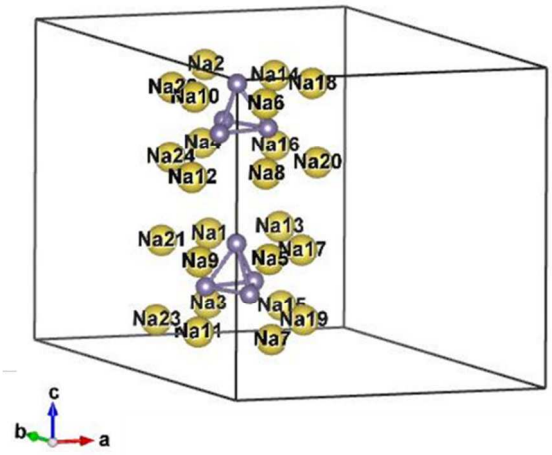


Figure S4. The cut-out of the atoms within the large channel in the staggered c×4 $Na_{32}Ge_{104}$ unit cell. The Na atoms are labeled by numbers.

In each of the four 6-memberred Na rings, there are two symmetrically unique Na atoms. From top to bottom, their distances to the *c*-axis are: 3.66 Å for Na2, 3.18 Å for Na6, 3.91 Å for Na12, 3.26 Å for Na16, 3.18 Å for Na1, 3.67 Å for Na5, 3.27 Å for Na11, and 3.90 Å for Na15. Certainly, as one Ge_4 tetrahedron rotates about the *c*-axis to be staggered to the other tetrahedron, the Na rings undergo a significant distortion, by ~0.5 Å radially to the *c*-axis, to accommodate the rotation. Without such a distortion, the staggered configuration is significantly higher in enthalpy than the eclipsed by 2.70 eV / unit cell. The associated large amplitude distortion of the Na rings kinetically hinders the eclipsed-to-staggered conversion of the tetrahedra arrangement.

Table S2: Select Ge-Ge distances in Na_4Ge_{13} and their corresponding crystal orbital Hamilton populations integrated to the Fermi level (–ICOHP).

pair	Distance (Å)	–ICOHP (eV / bond)
Ge1-Ge1	2.60	2.84
Ge1-Ge6	2.66	2.68
Ge2-Ge2	2.51	3.77
Ge2-Ge3	2.52	3.99
Ge2-Ge4	2.51	4.11
Ge3-Ge5	2.55	3.78
Ge4-Ge5	2.56,2.59	3.97, 3.57

Section S3. Calculated Band Structures and Densities of States of the $Na_{16}Ge_{52}$ unit cell.

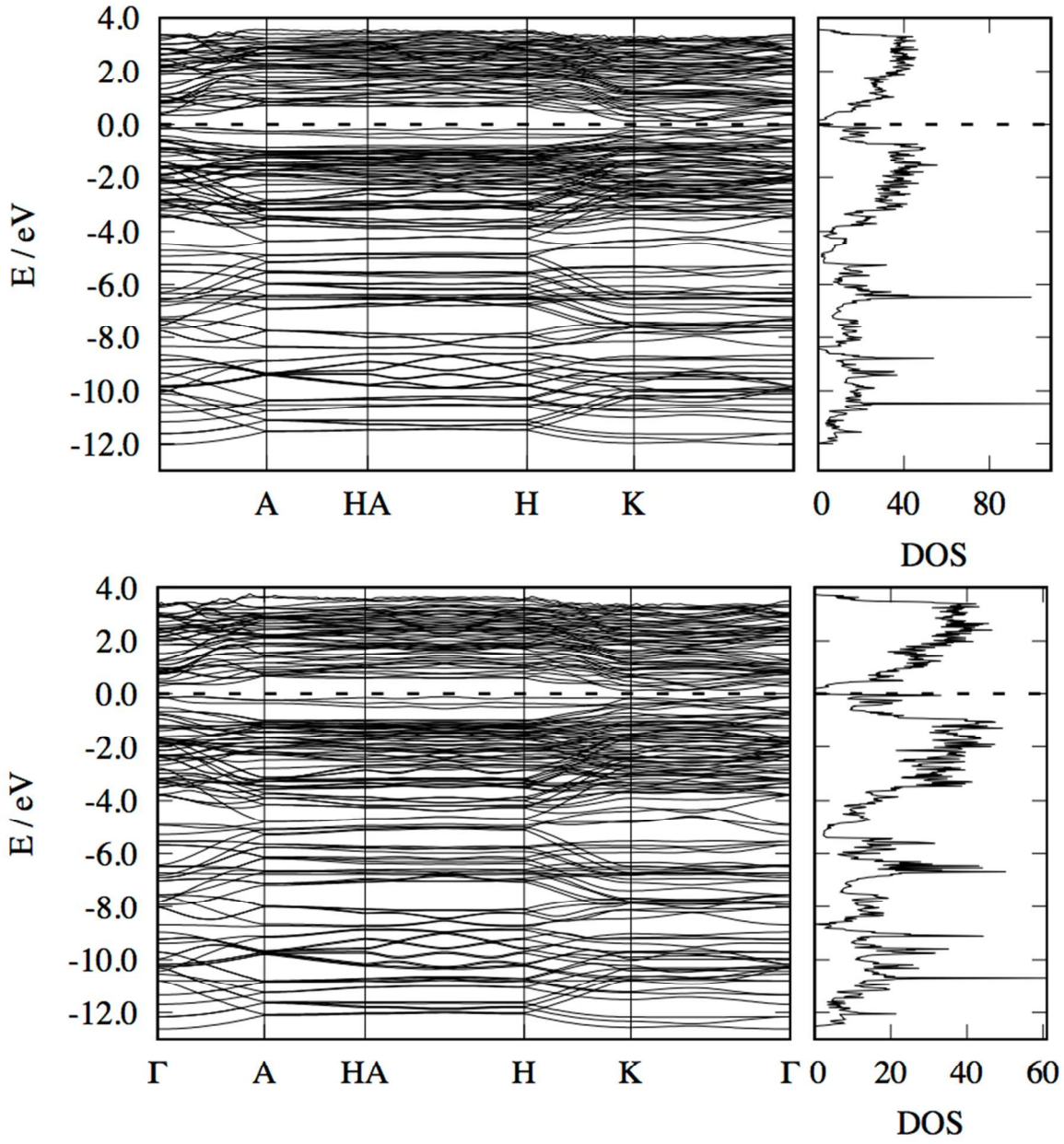


Figure S5. Band structure and DOS of the c×2 $Na_{16}Ge_{52}$ structure at 1 atm (upper panel) and 4 GPa (lower panel). They have been shifted so that the Fermi energy is at 0 eV.

Section S4. Thermal Conductivity of Na_4Ge_{13}.

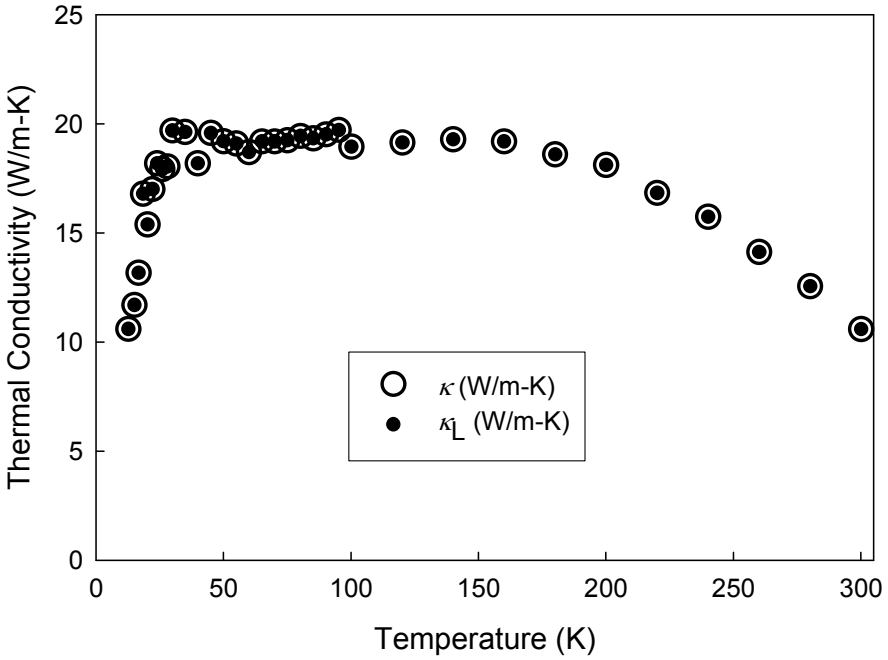


Figure S6. Total thermal conductivity, κ (open circles), and lattice contribution to the total thermal conductivity, κ_L (filled circles) for Na_4Ge_{13}.