Supporting Information

The Importance of Lone Pairs to Structure and Bonding of the novel Germanium Nitridophosphate GeP$_2$N$_4$

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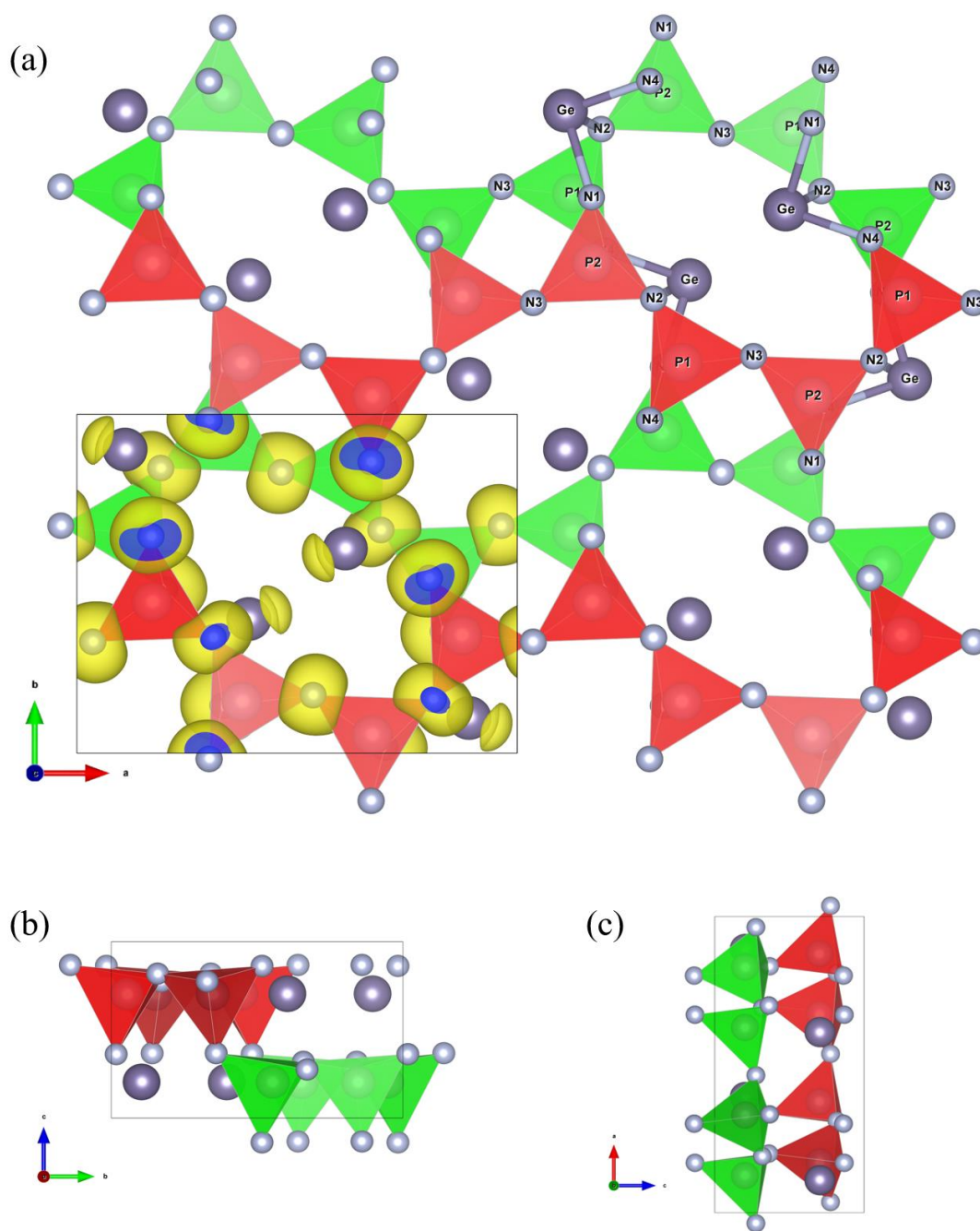
Figure S1. (a) A view of a 2x2x1 supercell of GeP_2N_4 along the c-axis is shown. The dimensions of the basis unit cell are indicated with a black box. PN_4 tetrahedra are shown in green and red throughout the diagram, which correspond to tetraheda centered in the lower or upper half of the unit cell along the c-axis, respectively. In the top right quadrant, each atom is labelled, and Ge-N bonds are shown. In the bottom left quadrant, an isocontour of the charge density of the uppermost valence band is shown. (b) A view of the unit cell along the a-axis. (c) A view of the unit cell along the b-axis.
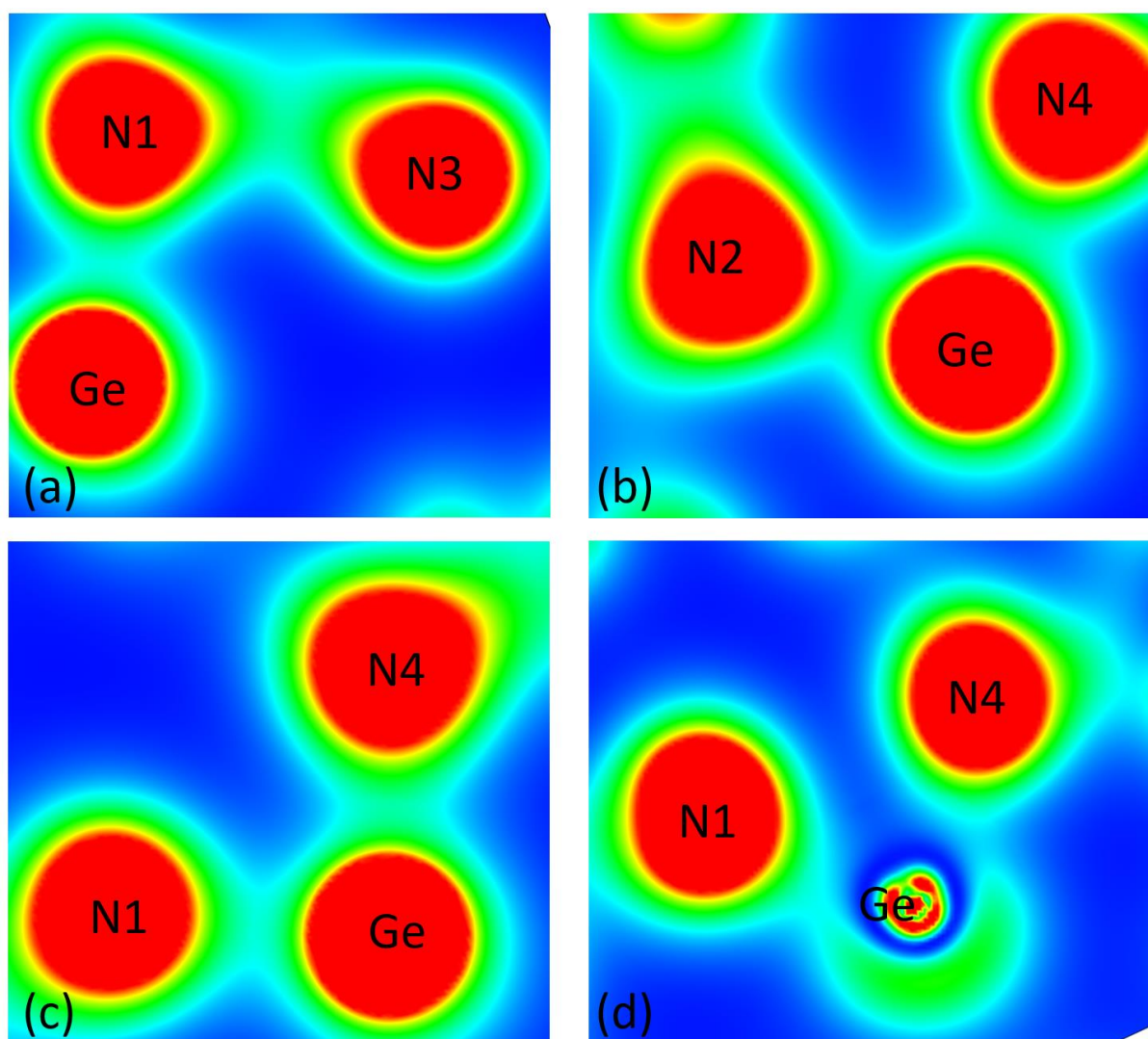

Figure S2. (a,b,c) A calculated total valence band charge density plot in a plane passing through the three labelled atoms as shown. (d) A calculated upper valence band charge density plot through the N1-Ge-N4 plane. This was selected to show the Ge lone pair.
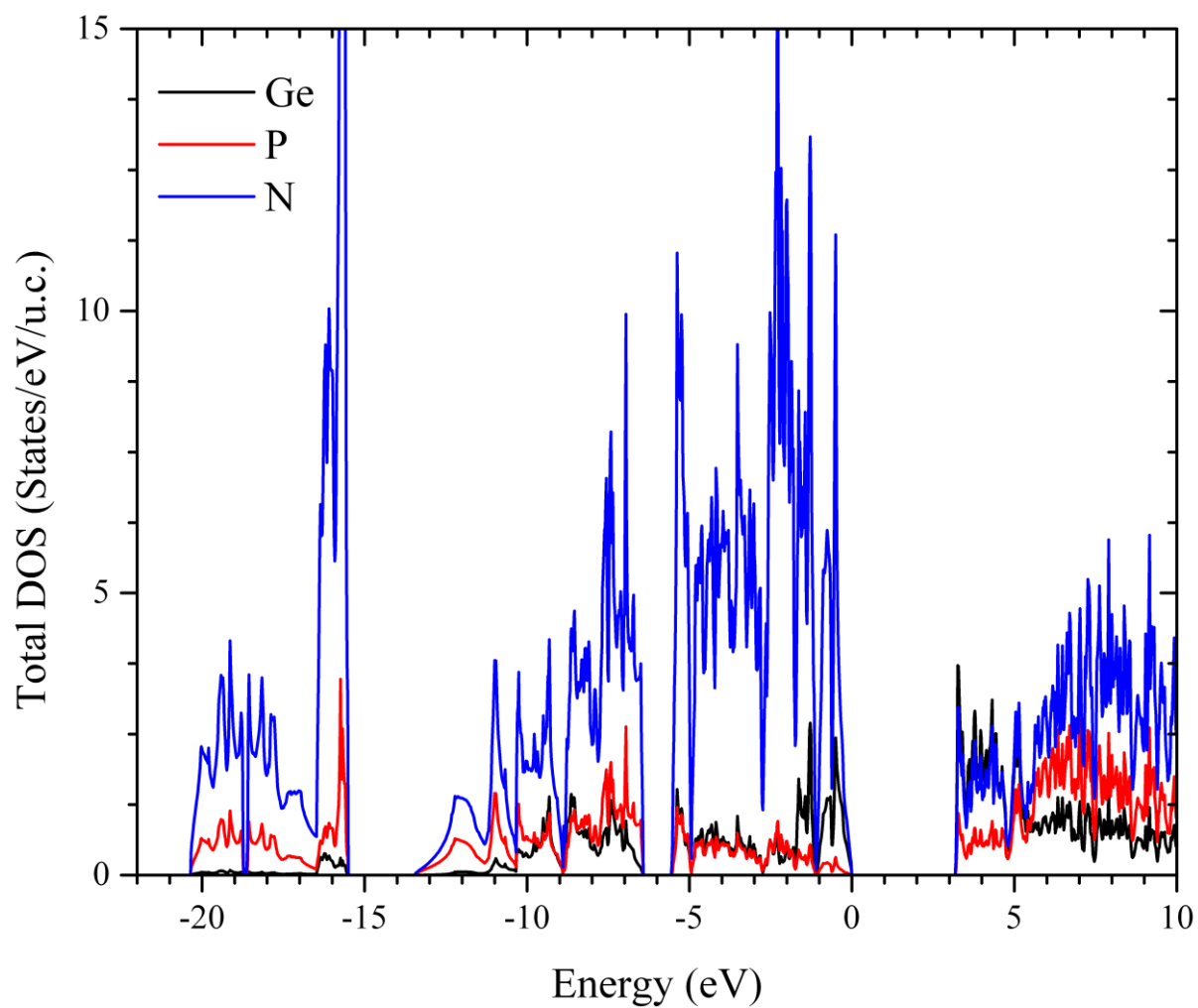
Figure S3. Total density of states of GeP_2N_4 summed over each atomic species in a unit cell.
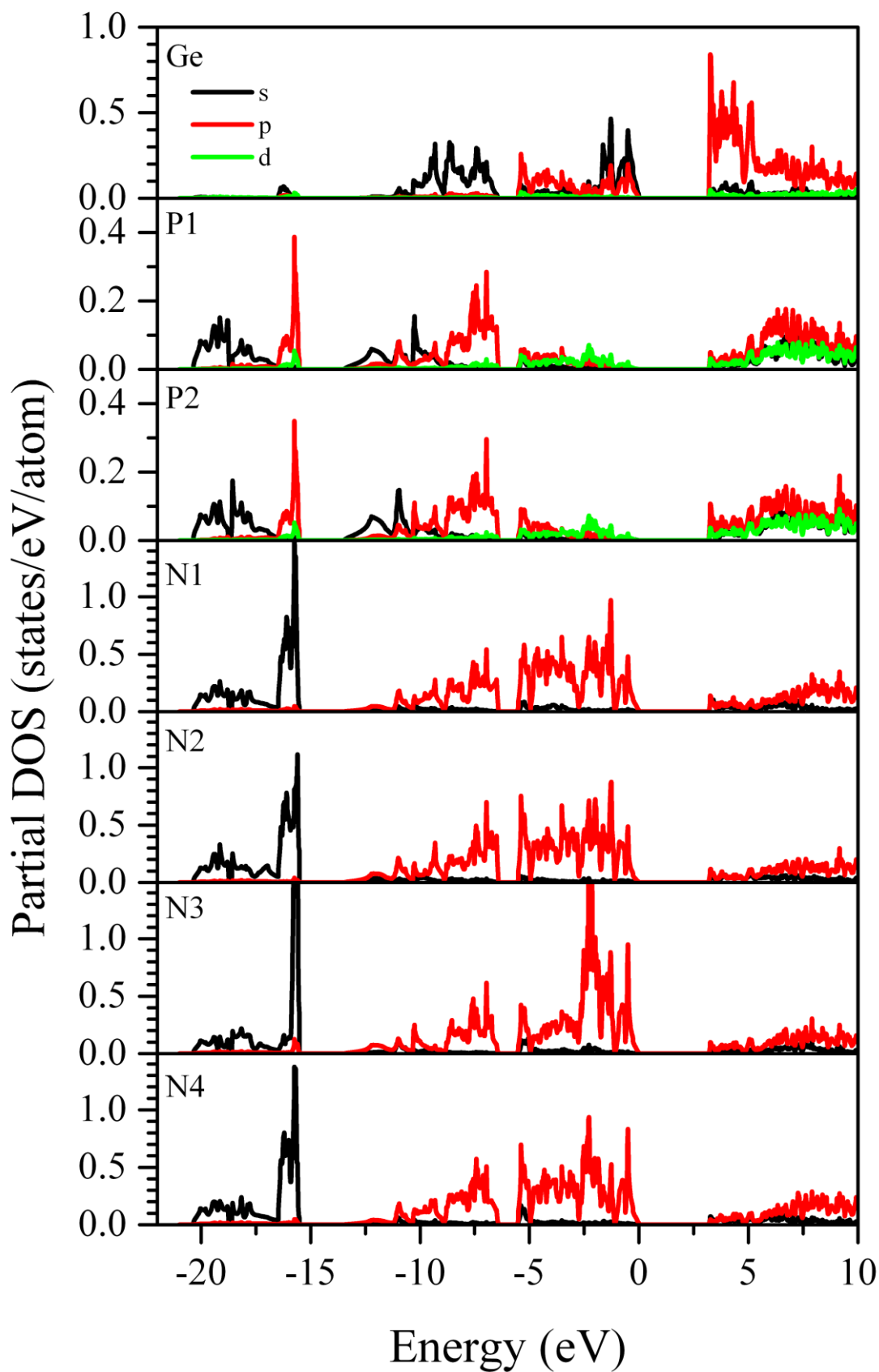
Figure S4. Calculated partial density of states (PDOS) of each atom in GeP$_2$N$_4$, with the atoms as labelled in each panel, and the orbital character as indicated. The calculation was performed with the PBE-GGA exchange-correlation functional.
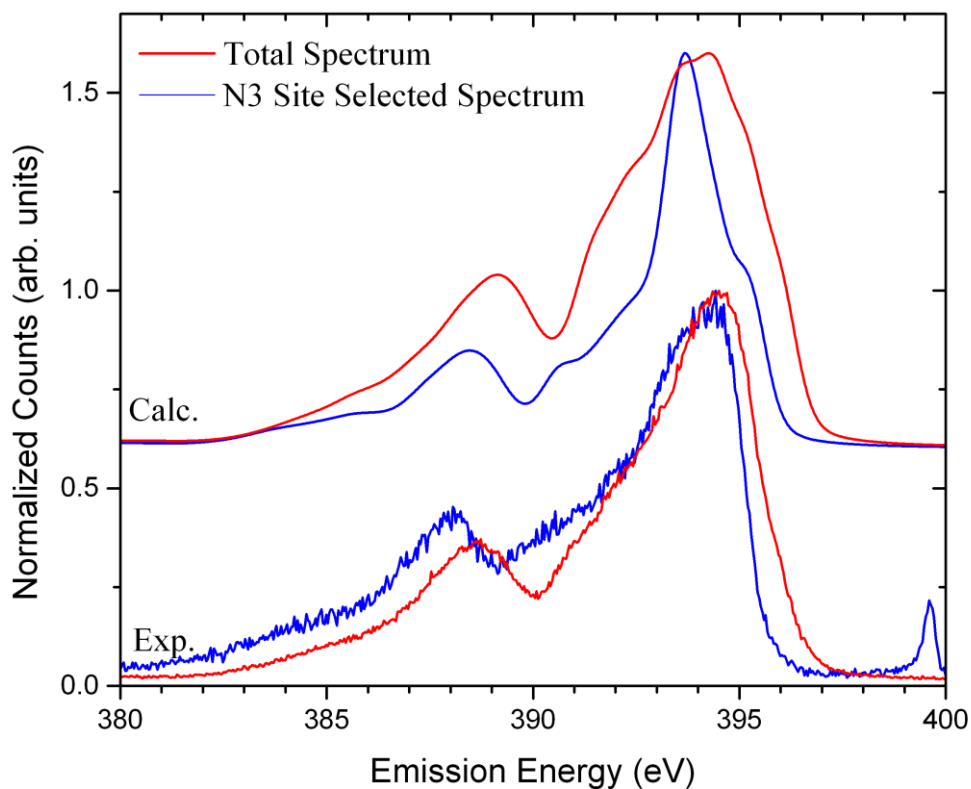
Figure S5. Experimental N K XES spectra of GeP_2N_4 are shown at the bottom of the panel. Non-resonant excitations are shown in red, and site-selective excitation of the N3 site at 399.6 eV is shown in blue. Above are calculated spectra of the N K emission of the combined unit cell compared with emission from only the N3 site. This site-selective excitation of the crystal is possible because the position of the 1s core level of the N3 site is 0.74 eV closer to the Fermi energy level than the other N sites.
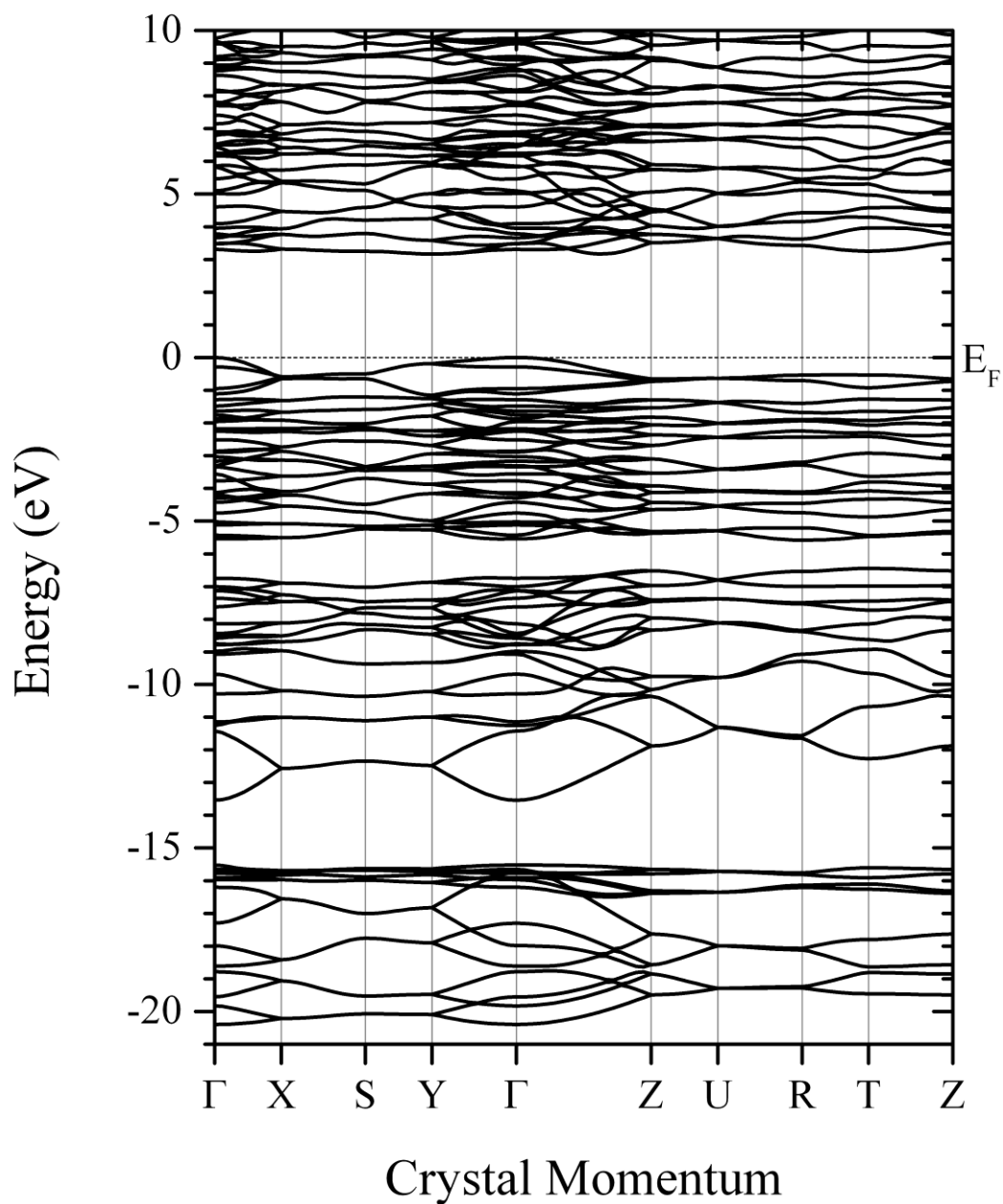
Figure S6. Band structure diagram of GeP_2N_4 calculated using the PBE-GGA exchange-correlation functional. The band gap is predicted to be *indirect*, with the valence band maximum at the Γ point and the conduction band minimum at the Y point.

Table S1. Crystallographic information of GeP_2N_4 from single crystal refinement. Standard deviations are given in parenthesis.

Parameter	GeP_2N_4
Crystal system	orthorhombic
Space group	$Pna2_1$ (no. 33)
Lattice parameters / Å	$a = 9.5468(12)$ $b = 7.5419(11)$ $c = 4.6941(6)$

Table S2. Wyckoff position, coordinates, isotropic thermal displacement parameters and occupancy of GeP_2N_4 from single-crystal refinement. Standard deviations are given in parenthesis. GeP_2N_4 crystallizes in the space group $Pna2_1$ (no. 33).

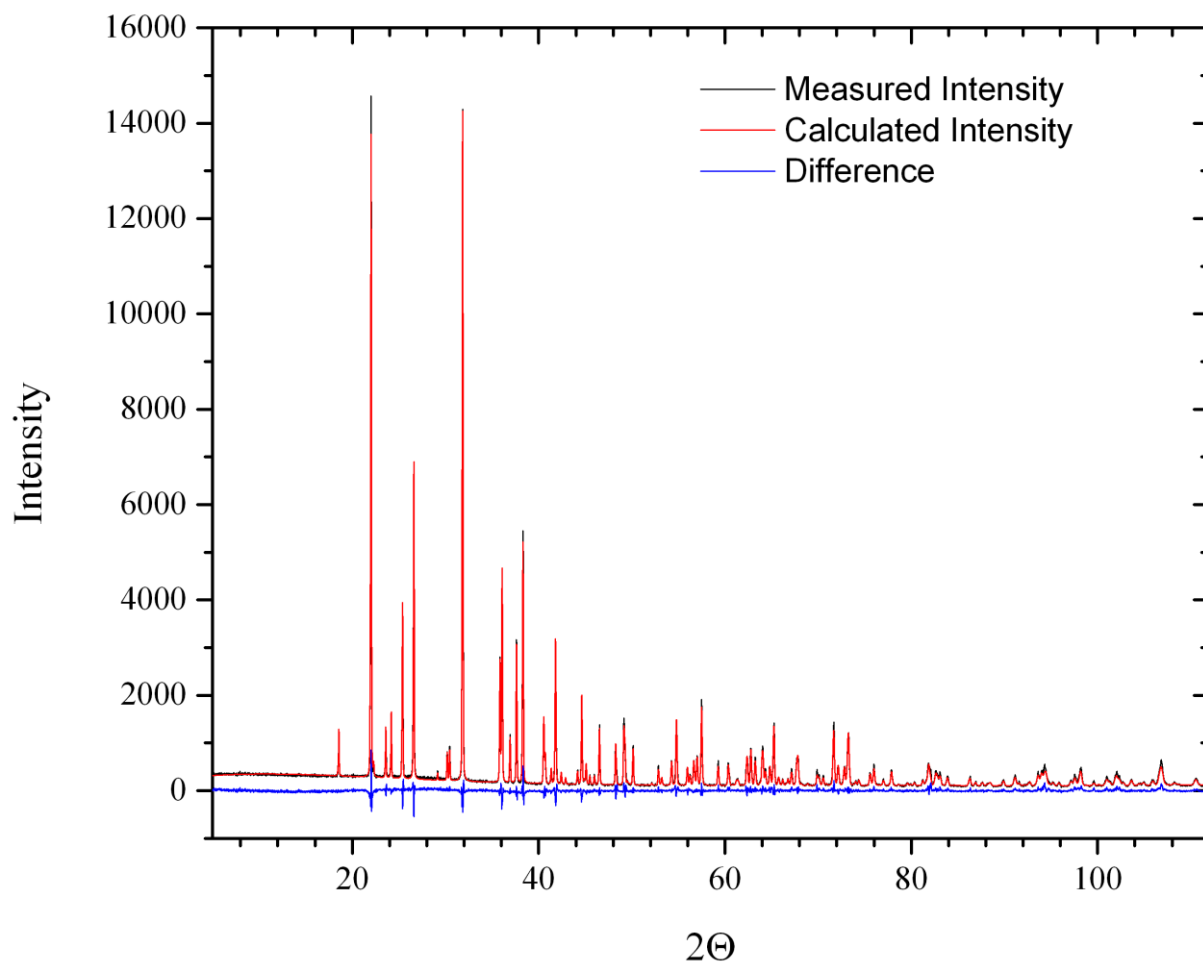| Atom	Wyck.	x	y	z	U_{eq}	*occ.*
Ge1	4*a*	0.89051(4)	0.10398(5)	0.2048(3)	0.00705(8)	1
P1	4*a*	0.87476(8)	0.34797(10)	0.7023(7)	0.00408(14)	1
P2	4*a*	0.67062(8)	0.0538(1)	0.7039(6)	0.00338(13)	1
N1	4*a*	0.8318(4)	0.3597(4)	0.3680(9)	0.0067(6)	1
N2	4*a*	0.8095(3)	0.1587(4)	−0.1809(9)	0.0048(6)	1
N3	4*a*	1.0361(3)	0.3287(5)	0.7757(9)	0.0070(7)	1
N4	4*a*	0.6996(4)	0.0169(4)	0.3625(9)	0.0053(6)	1

Figure S7. Powder X-ray diffraction data of GeP$_2$N$_4$ collected on a STOE Stadi P diffractometer) in modified Debye-Scherrer geometry with Cu-Kα_1 radiation (λ = 1.54060 Å). A calculated intensity is shown using Rietveld refinement.