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Supplementary materials
for

LOW PRESSURE METASTABLE SINGLE-BONDED SOLID NITROGEN PHASES

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These supplementary materials contain results that are mentioned or support those presented in the main text. Please note that figures and tables follow the text.

1. Convergence tests

The validity of the choice of the calculated parameters is demonstrated for the $P2_1$ nitrogen phase. First, consider the effect of kinetic energy cutoff (*ecut*) on the total energy. Since in this work we compare different solid atomic phases in terms of energy, *ecut* must be chosen in such a way that its further increase leads to a change in the total energy of less than 0.01 eV. Fig. S1 shows the behaviour of the difference in the total energy from *ecut*: $\Delta E(ecut) = |E_n(ecut + \Delta ecut) - E_n(ecut)|$, where $E_n(ecut)$ is the total energy of the structure at the current value of *ecut*, and $E_n(ecut+\Delta ecut)$ is the total energy of the structure with the value of kinetic energy cutoff increased by $\Delta ecut$ = 20 Ry. If *ecut* = 90 Ry is chosen, a further increase in *ecut* to 110 Ry changes the total energy by a value that does not exceed 0.005 eV in modulus. This accuracy is sufficient, therefore, all calculations in this work were performed with a kinetic energy cutoff equal to 90 Ry.

Also, the correct choice of k-point spacing Δk is necessary. Our test calculations for the $P2_1$ phase with *ecut* = 90 Ry show that as the value of $\Delta k \sim 0.025$Å^{-1} doubles, the total energy changes by less than 10^{-5} eV, and the elastic constants, which are more sensitive to the grid in k-space, change ≤ 0.5%. Thus, the choice of $\Delta k \leq 0.025$ Å^{-1} is sufficient for correct calculations.

2. Structural parameters of nitrogen structures

Table S1 lists the structural parameters of unit cells for molecular nitrogen crystals and the structure formed by 2 nitrogen clusters $N_8(C_{2v})$-B at zero pressure. Table S2 lists the structural parameters of unit cells for atomic nitrogen crystals at various pressures. Fig. S2 shows the relaxed crystal cells of various solid atomic phases of nitrogen. Table S3 lists data on bond lengths and bond angles for the $I2_13$, *Pccn*, $R\bar{3}$, and $P\bar{6}2c$ atomic nitrogen crystals at various pressures.

3. Dynamically unstable $P\bar{3}m1$ and *Pmmm* atomic phases of nitrogen and stable $R\bar{3}c$ cluster structure of nitrogen

Unit cells of unstable $P\bar{3}m1$, *Pmmm* phases and stable $R\bar{3}c$ cluster structure are shown in Fig. S3. Their structural parameters are presented in table S4. Table S5 lists the phonon frequencies at the Γ point for the *Pmmm* phase at a pressure of 380 GPa. Fig. S4 shows the phonon spectrum of the $P\bar{3}m1$ phase at a pressure of 160 GPa. The presence of imaginary frequencies indicates the dynamic instability of $P\bar{3}m1$ and *Pmmm* phases.

The $R\bar{3}c$ solid atomic phase of nitrogen transforms into a cluster structure with the same symmetry at pressures below 30 GPa. This transition is accompanied by an abrupt change in the volume per atom V_0. The increase in V_0 due to the transition of the structure from the solid state at a pressure of 30 GPa to the cluster form at a pressure of 20 GPa is $\Delta V_0 \approx 1.73$ Å^3/atom. For comparison, the increase in V_0 due to a decrease in pressure from 40 GPa to 30 GPa for the $R\bar{3}c$ solid atomic phase is ≈ 0.2 Å^3/atom. Fig. S5 shows the phonon spectrum and the phonon density of states for the $R\bar{3}c$ cluster structure at a

pressure of 20 GPa. The absence of imaginary frequencies in the phonon spectrum demonstrates the fulfillment of the dynamic stability criteria for this cluster phase. During the transition of the solid atomic structure of the $R\bar{3}c$ phase to the cluster form, a significant rearrangement of the phonon spectrum occurs, which can be seen when comparing Fig. S5 with Fig. 4 and Fig. 5 from the article.

4. Electron, phonon, and elastic properties of solid atomic phases of nitrogen

Figs. S6 and S7 show the phonon densities of states and the phonon free energy, respectively, for the $P2_1$ and $R\bar{3}c$ solid phases at different pressures. Fig. S8 shows the phonon densities of states for the $I2_13$, *Pccn*, and $R\bar{3}$ phases at zero pressure and $P = 100$ GPa, and for the $P\bar{6}2c$ phase at zero pressure and $P = 40$ GPa. The pressure of 40 GPa is the upper limit of the dynamic stability of the $P\bar{6}2c$ phase; therefore, in Fig. S8(d) (red curve), one can observe the presence of small non-zero values of the phonon density of states in the region of imaginary frequencies. Fig. S9 shows the dependences of the phonon free energy F_{ph} on temperature at various pressures for the $I2_13$, *Pccn*, $R\bar{3}$, and $P\bar{6}2c$ phases of nitrogen.

Fig. S10 shows the electronic band structures and electronic densities of states for the $I2_13$, *Pccn*, $R\bar{3}$, and $P\bar{6}2c$ phases at zero pressure.

The elastic properties for the $I2_13$ and *Pccn* phases are presented in Table S6, and the elastic properties for the $R\bar{3}$ and $P\bar{6}2c$ phases are presented in Table S7.

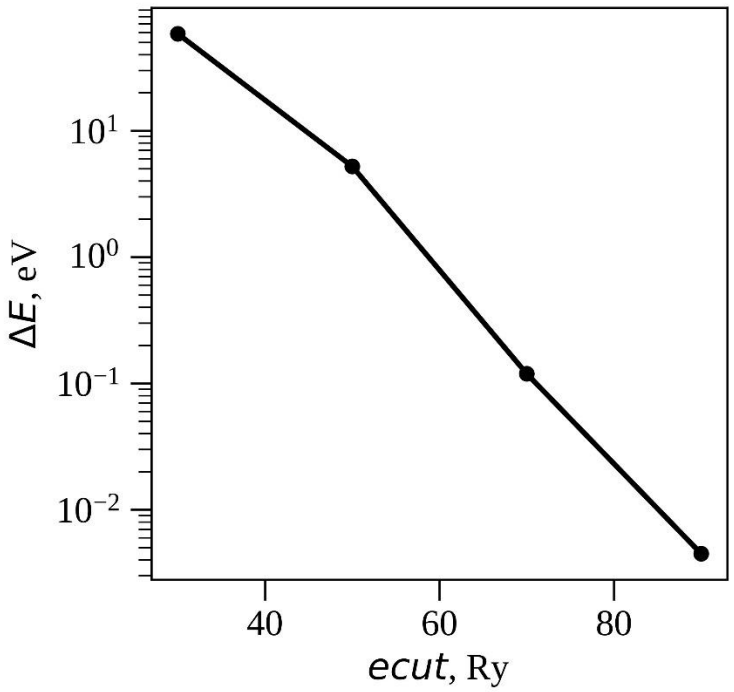

Figure S1. Difference in total energy for the $P2_1$ solid atomic nitrogen as a function of kinetic energy cutoff (ecut).

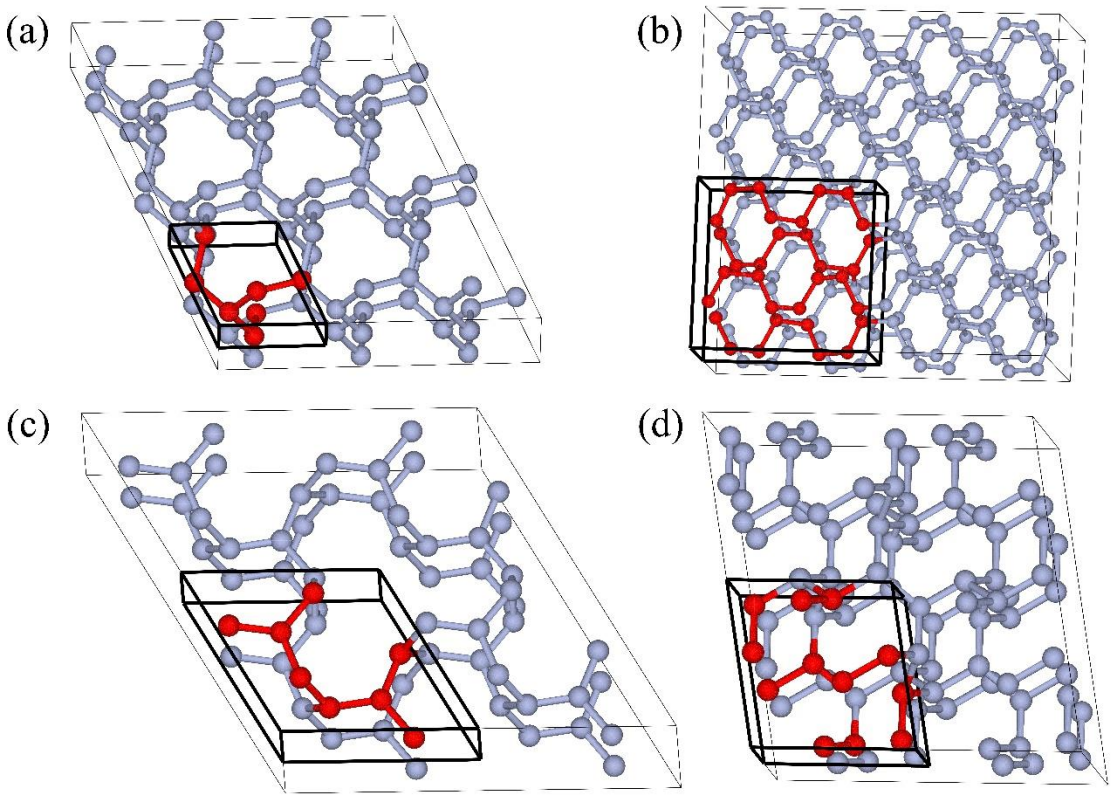

Figure S2. Crystal structures of different solid atomic phases of nitrogen at zero pressure: (a) $I2_13$, (b) *Pccn*, (c) $P\bar{6}2c$, and (d) $R\bar{3}$. Lattice is marked with a bold line and the atoms are marked in red.

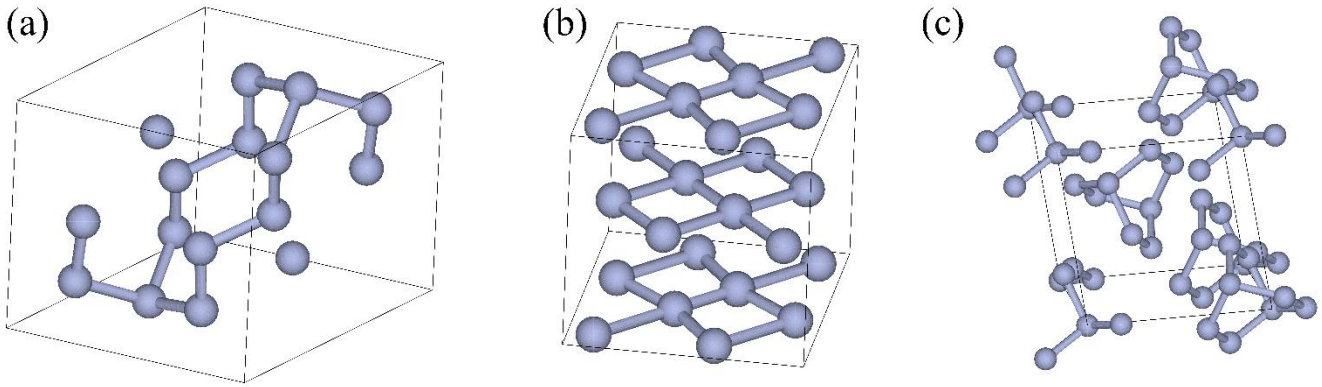

Figure S3. Unit cells of unstable atomic nitrogen phases (a) $P\bar{3}m1$, (b) *Pmmm*. (c) Unit cell of stable $R\bar{3}c$ cluster structure.

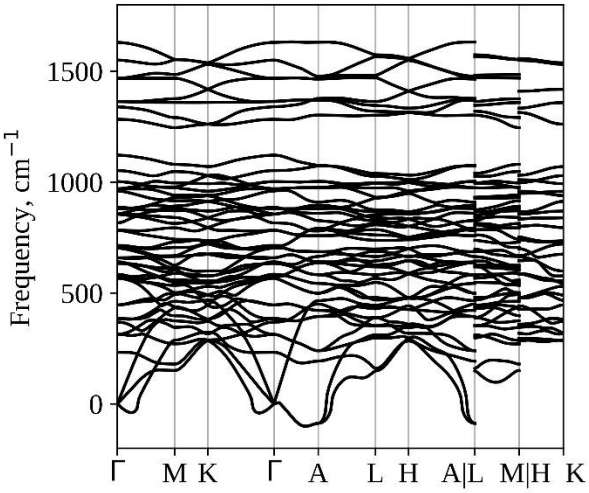

Figure S4. Phonon spectrum of the $P\bar{3}m1$ phase at a pressure of 160 GPa.

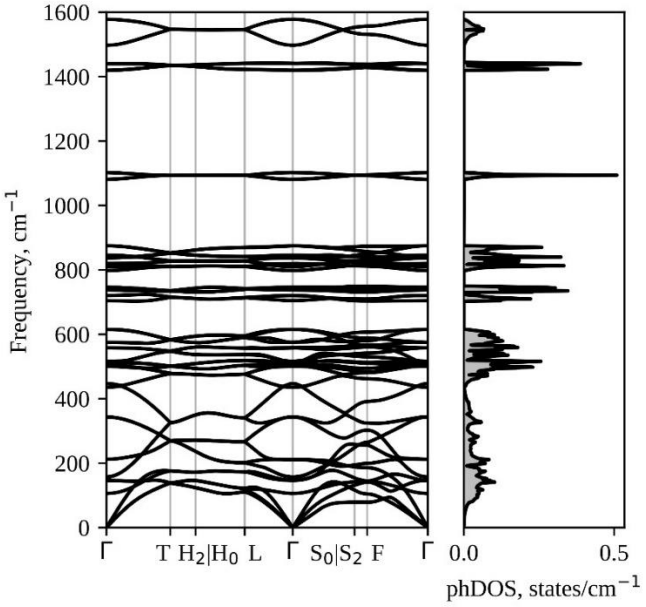

Figure S5. Phonon spectrum and phonon density of states for the $R\bar{3}c$ cluster structure at a pressure of 20 GPa.

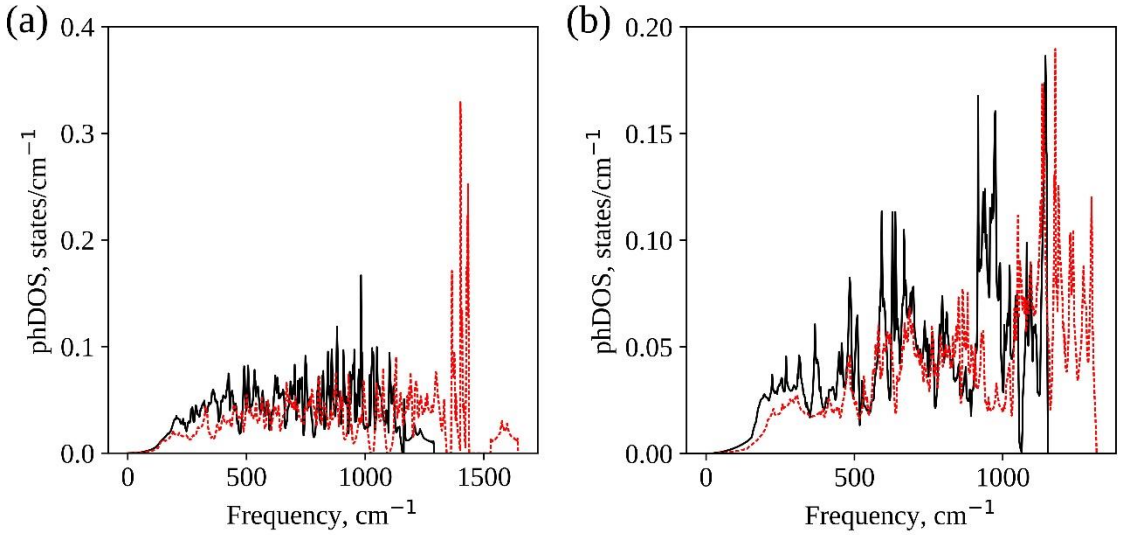

Figure S6. Phonon densities of states: (a) $P2_1$ phase, black curve corresponds to zero pressure, red curve corresponds to a pressure of 100 GPa; (b) $R\bar{3}c$ solid atomic phase, black curve corresponds to a pressure of 30 GPa, red curve corresponds to a pressure of 100 GPa.

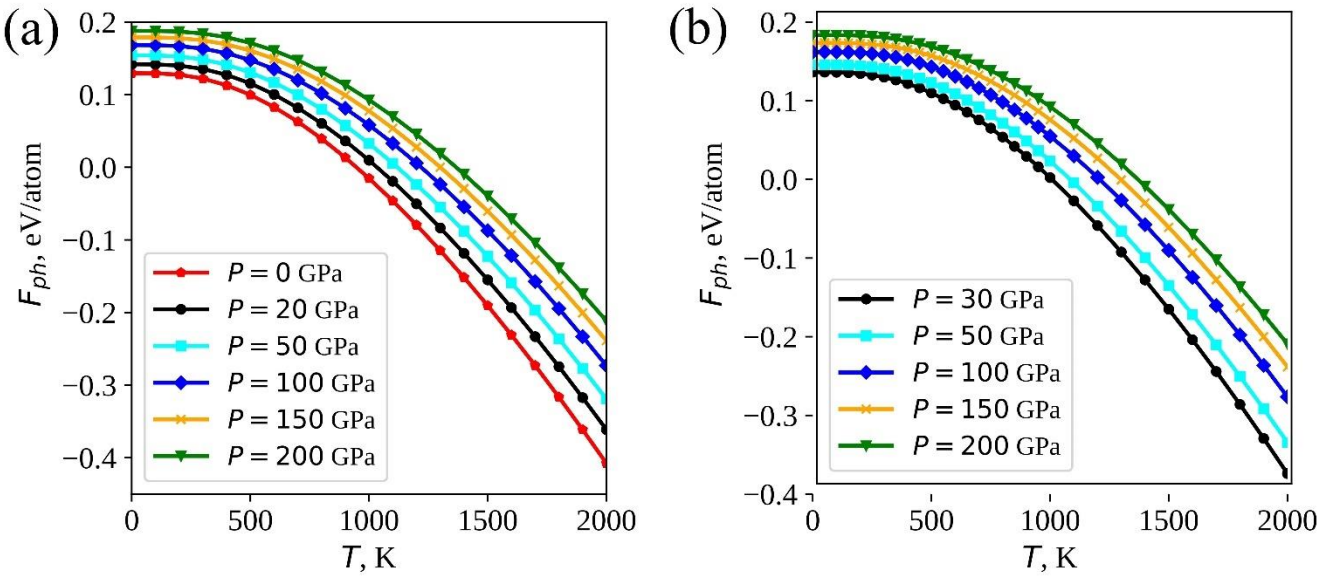

Figure S7. Temperature dependence of the phonon free energy F_{ph} at various pressures for solid atomic phases of nitrogen (a) $P2_1$; (b) $R\bar{3}c$.

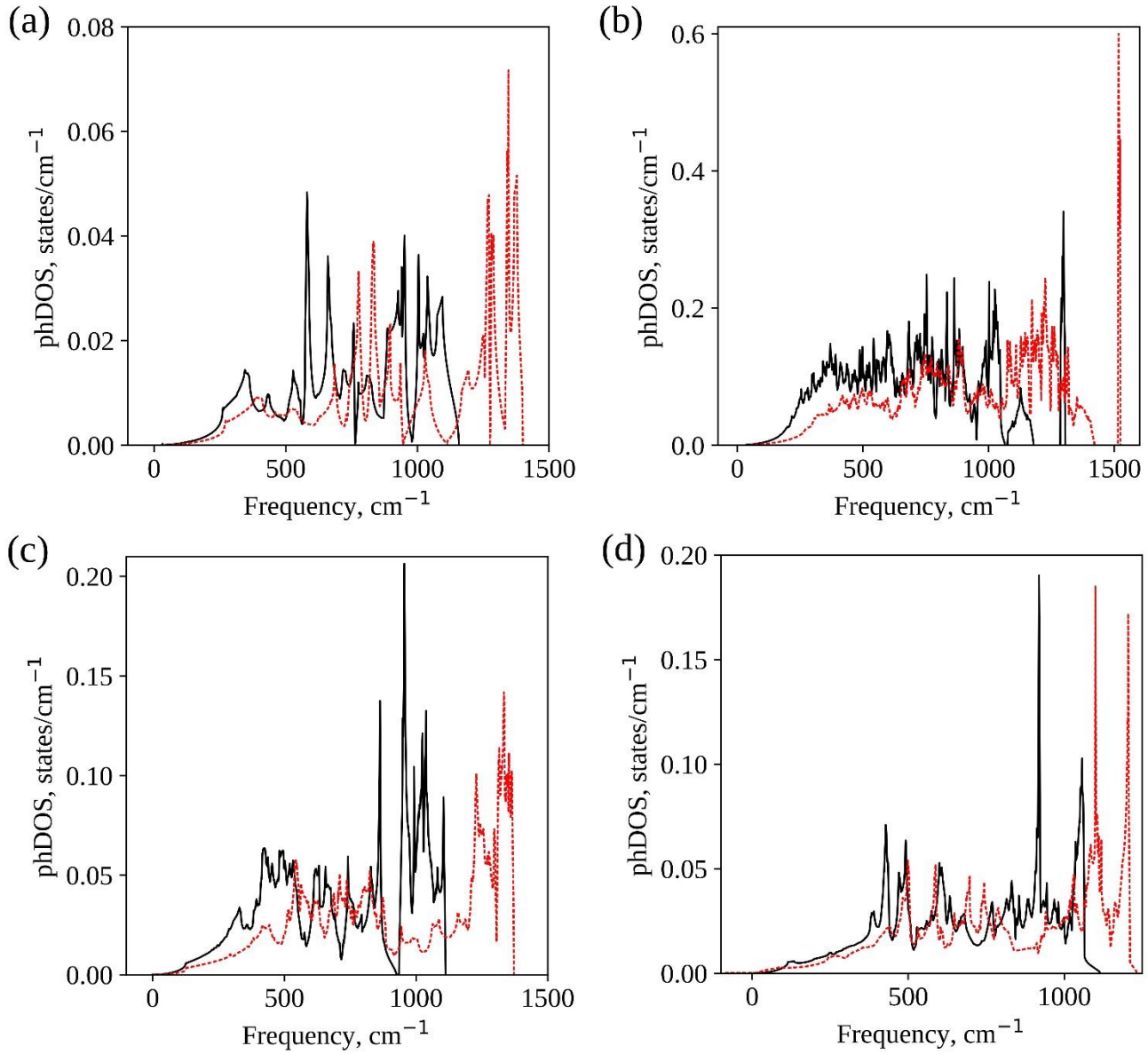

Figure S8. Phonon density of states for different solid nitrogen phases: (a) $I2_13$; (b) *Pccn*; (c) $R\bar{3}$; (d) $P\bar{6}2c$. The black curve corresponds to zero pressure, the red curve corresponds to a pressure of 100 GPa for (a)-(c), and a pressure of 40 GPa for (d).

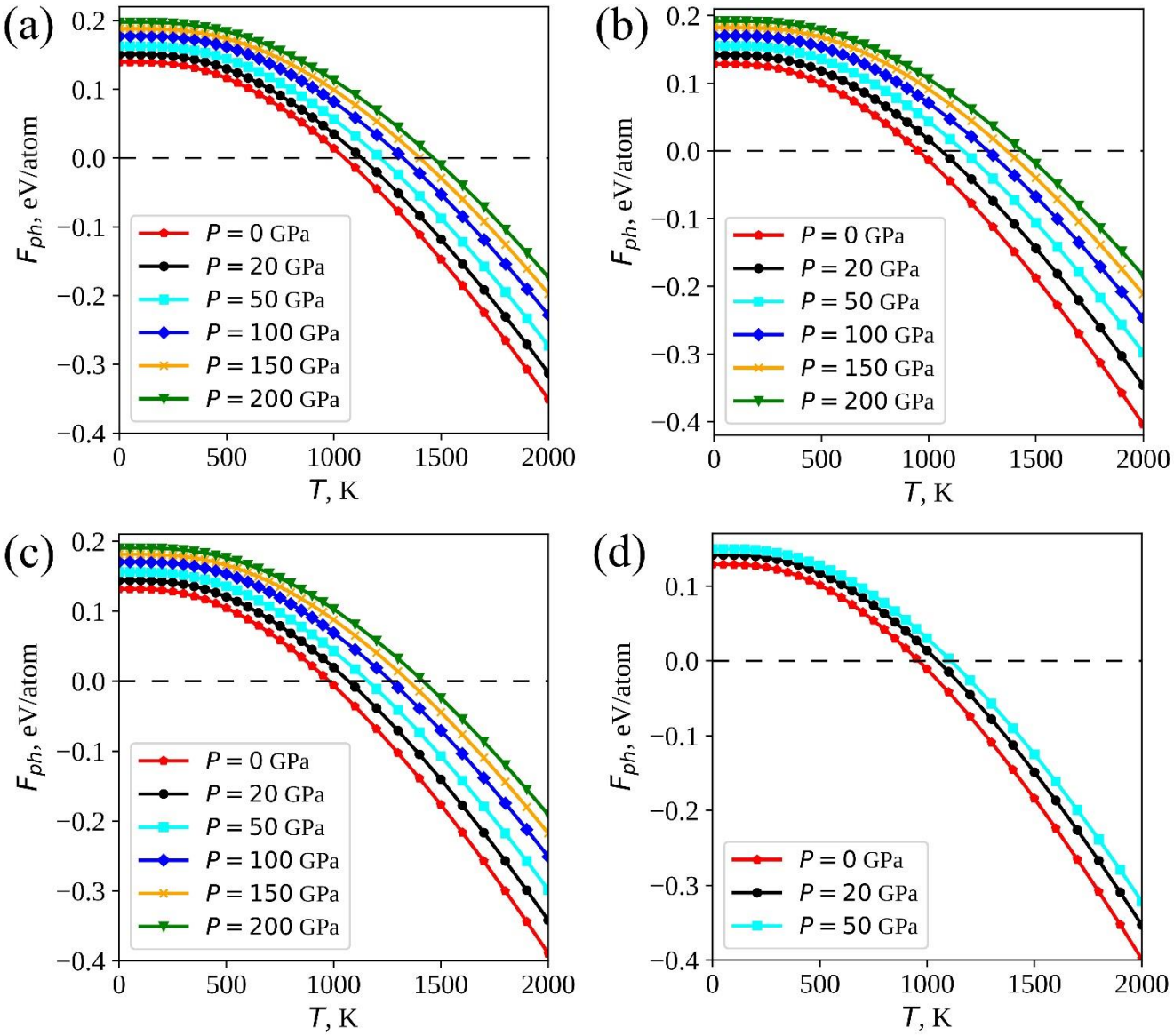

Figure S9. Temperature dependence of phonon free energy for solid atomic phases of nitrogen: (a) $I2_13$; (b) $Pccn$; (c) $R\bar{3}$; (d) $P\bar{6}2c$.

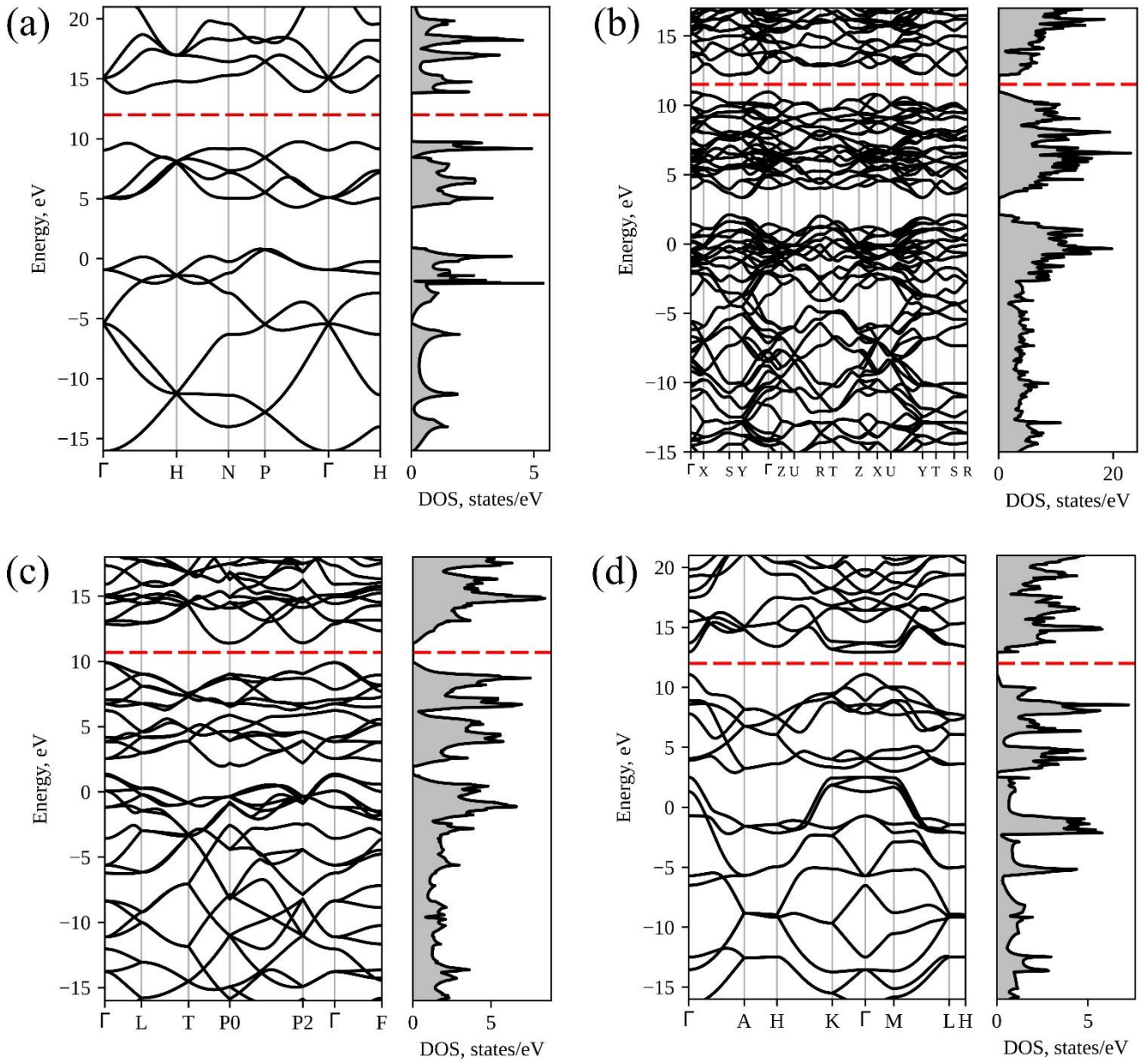

Figure S10. Electronic band structure and electronic density of states at zero pressure for nitrogen atomic phases: (a) $I2_13$, (b) *Pccn,* (c) $R\bar{3}$, (d) $P\bar{6}2c$. The red dotted line shows the position of the Fermi level.

Table S1. Structural parameters of the relaxed nitrogen molecular crystals and crystal formed from two $N_8(C_{2v})$-B nitrogen clusters at zero pressure.

Symmetry/ Pressure/ No. Atoms	Lattice parameters (Å, °)	Atomic coordinates (fractional)
$P6_3/mmc$ (molecular) P = 0 GPa 16 atoms	a = b = 8.47273, c = 6.88605; α = β = 90.0, γ = 120.0	N 0.16667 0.33333 0.33006 N 0.83333 0.66667 0.66994 N 0.66667 0.83333 0.33006 N 0.33333 0.16667 0.66994 N 0.16667 0.83333 0.33006 N 0.83333 0.16667 0.66994 N 0.83333 0.66667 0.83006 N 0.16667 0.33333 0.16994 N 0.33333 0.16667 0.83006 N 0.66667 0.83333 0.16994 N 0.83333 0.16667 0.83006 N 0.16667 0.83333 0.16994 N 0.66667 0.33333 0.33006 N 0.33333 0.66667 0.66994 N 0.33333 0.66667 0.83006 N 0.66667 0.33333 0.16994
$R\bar{3}c$ (molecular) P = 0 GPa 16 atoms	a = b = c = 7.78341; α = β = γ = 86.49329	N 0.03262 0.55181 0.70934 N 0.29066 0.96738 0.44819 N 0.55181 0.70934 0.03262 N 0.96141 0.96141 0.96141 N 0.05181 0.53262 0.20934 N 0.46738 0.79066 0.94819 N 0.44819 0.29066 0.96738 N 0.03859 0.03859 0.03859 N 0.94819 0.46738 0.79066 N 0.53859 0.53859 0.53859 N 0.96738 0.44819 0.29066 N 0.46141 0.46141 0.46141 N 0.70934 0.03262 0.55181 N 0.79066 0.94819 0.46738 N 0.53262 0.20934 0.05181 N 0.20934 0.05181 0.53262
$P4_2/mnm$ (molecular) P = 0 GPa 16 atoms	a = b = 8.55189, c = 5.53948; α = β = 90.0, γ = 89.99969	N 0.04557 0.04557 0.00000 N 0.95443 0.95443 0.00000 N 0.20443 0.29557 0.50000 N 0.29557 0.20443 0.50000 N 0.04557 0.54557 0.00000 N 0.95443 0.45443 0.00000 N 0.70443 0.29557 0.50000 N 0.79558 0.20443 0.50000 N 0.20443 0.79557 0.50000 N 0.29558 0.70443 0.50000

		N 0.54557 0.04557 0.00000 N 0.45443 0.95443 0.00000 N 0.54557 0.54557 0.00000 N 0.45443 0.45443 0.00000 N 0.70443 0.79557 0.50000 N 0.79557 0.70443 0.50000
*P*1 cluster $N_8(C_{2v})$-B *P* = 0 GPa 16 atoms	a = 5.48339, b = 5.59300, c = 7.31683; α = 102.79741, β = 89.99073, γ = 90.00651	N 0.23511 -0.05156 0.08603 N 0.25613 0.07792 -0.03165 N 0.03269 -0.00604 0.20652 N 0.07316 0.25520 -0.03167 N -0.17234 -0.20504 -0.05060 N -0.15144 -0.07570 -0.16838 N -0.16916 -0.08212 0.13921 N -0.12835 0.17852 -0.09896 N 0.73512 0.53641 0.41647 N 0.75612 0.40698 0.53418 N 0.53271 0.49081 0.29600 N 0.57315 0.22967 0.53424 N 0.32765 0.68986 0.55312 N 0.34853 0.56057 0.67093 N 0.33085 0.56687 0.36332 N 0.37163 0.30634 0.60155

Table S2. Structural parameters of the relaxed atomic nitrogen crystal structures.

Symmetry/Pressure/ No. Atoms	Lattice parameters (Å, °)	Atomic coordinates (fractional)
$P2_1$ *P* = 0 GPa 16 atoms	a = 3.37970, b = 6.19363, c = 5.81349; α = 108.98952, β = 90.0, γ = 90.0	N 0.34907 0.06960 0.27752 N 0.29277 0.11501 0.06471 N 0.15576 -0.12404 0.32188 N -0.03769 0.23567 0.01541 N -0.05066 -0.26805 -0.11489 N -0.26331 -0.12632 -0.23253 N -0.08941 -0.24931 0.11716 N -0.39228 0.08855 -0.09192 N 0.84907 0.40609 0.22111 N 0.79277 0.36068 0.43392 N 0.65575 0.59973 0.17674 N 0.46231 0.24002 0.48322 N 0.44934 0.74374 0.61352 N 0.23669 0.60201 0.73116 N 0.41059 0.72500 0.38147 N 0.10772 0.38714 0.59055
$R\bar{3}c$ *P* = 30 GPa 16 atoms	a = b = c = 4.76941; α = β = γ = 74.99470	N 0.02854 0.58485 0.83803 N 0.16197 0.97146 0.41515 N 0.58485 0.83803 0.02854

		N 0.87245 0.87245 0.87245 N 0.08485 0.52854 0.33803 N 0.47146 0.66197 0.91515 N 0.41515 0.16197 0.97146 N 0.12755 0.12755 0.12755 N 0.91515 0.47146 0.66197 N 0.62755 0.62755 0.62755 N 0.97146 0.41515 0.16197 N 0.37245 0.37245 0.37245 N 0.83803 0.02854 0.58485 N 0.66197 0.91515 0.47146 N 0.52854 0.33803 0.08485 N 0.33803 0.08485 0.52854
$I2_13$ P = 0 GPa 4 atoms	a = b = c = 3.27198; α = β = γ = 109.47122	N 0.17124 0.17124 0.17124 N 0.50000 1.00000 0.32876 N 1.00000 0.32876 0.50000 N 0.32876 0.50000 1.00000
Pccn P = 0 GPa 32 atoms	a = 7.66217, b = 3.77843, c = 7.37328; α = β = γ = 90.0	N 0.17566 0.83301 0.55025 N 0.82434 0.16699 0.44975 N 0.32434 0.66699 0.55025 N 0.67566 0.33301 0.44975 N 0.82434 0.33301 0.94975 N 0.17566 0.66699 0.05025 N 0.67566 0.16699 0.94975 N 0.32434 0.83301 0.05025 N 0.66279 0.64428 0.54204 N 0.33721 0.35572 0.45796 N 0.83721 0.85572 0.54204 N 0.16279 0.14428 0.45796 N 0.33721 0.14428 0.95796 N 0.66279 0.85572 0.04204 N 0.16279 0.35572 0.95796 N 0.83721 0.64428 0.04204 N 0.41579 0.42984 0.28057 N 0.58421 0.57016 0.71943 N 0.08421 0.07016 0.28057 N 0.91579 0.92984 0.71943 N 0.58421 0.92984 0.21943 N 0.41579 0.07016 0.78057 N 0.91579 0.57016 0.21943 N 0.08421 0.42984 0.78057 N 0.91786 0.20672 0.26713 N 0.08214 0.79328 0.73287 N 0.58214 0.29328 0.26713 N 0.41786 0.70672 0.73287 N 0.08214 0.70672 0.23287 N 0.91786 0.29328 0.76713 N 0.41786 0.79328 0.23287 N 0.58214 0.20672 0.76713

$R\bar{3}$ P = 0 GPa 12 atoms	a = b = c = 4.45727; α = β = γ = 98.32226	N 0.93044 0.59422 0.39121 N 0.06956 0.40578 0.60879 N 0.39121 0.93044 0.59422 N 0.60879 0.06956 0.40578 N 0.59422 0.39121 0.93044 N 0.40578 0.60879 0.06956 N 0.89121 0.43044 0.09422 N 0.10879 0.56956 0.90578 N 0.09422 0.89121 0.43044 N 0.90578 0.10879 0.56956 N 0.43044 0.09422 0.89121 N 0.56956 0.90578 0.10879
$P\bar{6}2c$ P = 0 GPa 8 atoms	a = b = 5.24366, c = 2.33377; α = β = 90.0, γ = 120.0	N 0.71168 0.09367 0.25000 N 0.90633 0.61801 0.25000 N 0.38199 0.28832 0.25000 N 0.28832 0.38199 0.75000 N 0.61801 0.90633 0.75000 N 0.09367 0.71168 0.75000 N 0.66667 0.33333 0.25000 N 0.33333 0.66667 0.75000

Table S3. Bond lengths (L_{bond}), bond angles (α_{bond}), and volume per atom (V_0) for solid atomic nitrogen crystals at various pressures. The mean value of a quantity is denoted by <...>.

Symmetry/ No. atoms	P, GPa	L_{bond}, Å	α_{bond}, °	V_0, Å^3/atom
Pccn 32 atoms	0	1.301...1.557 <L_{bond}>=1.431	107.9...119.3 <α_{bond}>=112.7	6.67
	50	1.288...1.437 <L_{bond}>=1.384	105.3...119.7 <α_{bond}>=110.9	5.72
	100	1.276...1.395 <L_{bond}>=1.357	103.4...119.1 <α_{bond}>=109.7	5.21
$R\bar{3}$ 12 atoms	0	1.390, 1.498	114.4, 108.2, 112.7	7.12
	50	1.373, 1.409	112.9, 105.2, 109.2	6.00
	100	1.357, 1.371	112.2, 103.4, 106.8	5.40
$P\bar{6}2c$ 8 atoms	0	1.390, 1.444	117.5, 107.8, 120.0	6.95
	40	1.359, 1.396	115.8, 108.5, 120.0	5.93

Table S4. Structural parameters of the unstable *Pmmm* and $P\bar{3}m1$ atomic phases of nitrogen, and stable $R\bar{3}c$ cluster structure.

Symmetry/ Pressure/ No. Atoms	Lattice parameters (Å, °)	Atomic coordinates (fractional)
Pmmm 380 GPa 16 atoms	a = b = 3.95736, c = 3.86057; α = β = 90.0, γ = 86.41625	N 0.10901 0.10901 0.00000 N 0.89099 0.89099 0.00000 N 0.12334 0.37666 0.50000 N 0.37666 0.12334 0.50000 N 0.10901 0.60901 -0.00000 N 0.89099 0.39099 -0.00000 N 0.62341 0.37659 0.50000 N 0.87659 0.12341 0.50000 N 0.12341 0.87659 0.50000 N 0.37659 0.62341 0.50000 N 0.60901 0.10901 0.00000 N 0.39099 0.89099 0.00000 N 0.60901 0.60901 0.00000 N 0.39099 0.39099 0.00000 N 0.62334 0.87666 0.50000 N 0.87666 0.62334 0.50000
$P\bar{3}m1$ 160 GPa 16 atoms	a=b=4.27693, c=4.80669; α = β = 90.0, γ = 120.0	N 0.16935 0.33870 0.43868 N 0.83065 0.66130 0.56132 N 0.66130 0.83065 0.43868 N 0.33870 0.16935 0.56132 N 0.16935 0.83065 0.43868 N 0.83065 0.16935 0.56132 N 0.84337 0.68675 0.82025 N 0.15663 0.31325 0.17975 N 0.31325 0.15663 0.82025 N 0.68675 0.84337 0.17975 N 0.84337 0.15663 0.82025 N 0.15663 0.84337 0.17975 N 0.66667 0.33333 0.19516 N 0.33333 0.66667 0.80484 N 0.33333 0.66667 1.06145 N 0.66667 0.33333 -0.06145
$R\bar{3}c$ (cluster) 20 GPa 16 atoms	a=b=c=5.17443; α = β = γ = 75.12449	N 0.01570 0.60032 0.80105 N 0.19895 0.98430 0.39968 N 0.60032 0.80105 0.01570 N 0.86256 0.86256 0.86256 N 0.10032 0.51570 0.30105 N 0.48430 0.69895 0.89968 N 0.39968 0.19895 0.98430 N 0.13744 0.13744 0.13744 N 0.89968 0.48430 0.69895 N 0.63744 0.63744 0.63744

		N 0.98430 0.39968 0.19895 N 0.36256 0.36256 0.36256 N 0.80105 0.01570 0.60032 N 0.69895 0.89968 0.48430 N 0.51570 0.30105 0.10032 N 0.30105 0.10032 0.51570

Tables S5 Phonon frequencies at Γ point of the unstable *Pmmm* atomic phase of nitrogen at pressure of 380 GPa.

Phonon frequencies at Γ point (cm^{-1})
-939.49, -638.64, -441.19, 0.00, 0.00, 0.00, 90.63, 135.50, 249.21, 261.11, 261.20, 390.37, 390.43, 411.45, 552.41, 573.88, 573.89, 582.94, 691.83, 710.91, 739.02, 774.20, 774.70, 811.17, 811.25, 849.27, 856.01, 856.21, 866.60, 900.38, 900.67, 1102.95,1103.93, 1117.87, 1117.97, 1192.91, 1212.49, 1241.44, 1418.71, 1424.45, 1425.01, 1453.59, 1482.90, 1483.71, 1491.13, 1492.24, 1768.65, 1768.69

Table S6 Mechanical properties of the $I2_13$ and *Pccn* solid atomic phases of nitrogen.

	***I*2$_1$3**					***Pccn***				
P, GPa	0	50	100	150	200	0	50	100	150	200
B, GPa	284	451	610	761	910	203	449	623	782	935
S, GPa	253	322	368	399	418	223	329	392	442	482
E, GPa	585	780	920	1019	1086	490	794	973	1115	1232
n	0.16	0.21	0.25	0.28	0.30	0.10	0.21	0.24	0.26	0.28
B/*S*	1.12	1.40	1.66	1.91	2.18	0.91	1.36	1.59	1.77	1.94
A^U	0.16	0.00	0.08	0.35	0.78	0.10	0.12	0.28	0.54	0.88
A_B, %	0.0	0.0	0.0	0.0	0.0	0.5	0.3	0.2	0.1	0.1
A_S, %	1.6	0.0	0.8	3.3	7.2	0.9	1.1	2.7	5.1	8.0

Table S7 Mechanical properties of the $R\bar{3}$ and $P\bar{6}2c$ solid atomic phases of nitrogen.

	$\boldsymbol{R\bar{3}}$					$\boldsymbol{P\bar{6}2c}$				
P, GPa	0	50	100	150	200	0	10	20	30	40
B, GPa	214	417	581	737	888	178	231	282	329	375
S, GPa	188	256	313	369	424	127	131	132	129	124
E, GPa	436	635	793	946	1095	306	328	337	333	320
n	0.16	0.24	0.27	0.28	0.29	0.21	0.25	0.27	0.29	0.29
B/*S*	1.14	1.63	1.86	2.00	2.09	1.40	1.76	2.14	2.55	3.02
A^U	2.79	2.61	2.45	2.22	2.00	3.31	5.03	7.82	13.07	26.49
A_B, %	10.0	4.5	3.3	2.7	2.2	7.7	6.1	5.0	4.2	3.6
A_S, %	20.4	20.1	19.2	17.8	16.3	23.9	32.9	43.6	56.5	72.5