

Electronic Supplementary Information for
“ Semiconductor-to-Metal Reconstructive Phase
Transition and Superconductivity of Anti-perovskite
 Ca_3PN under Hydrostatic Pressure”

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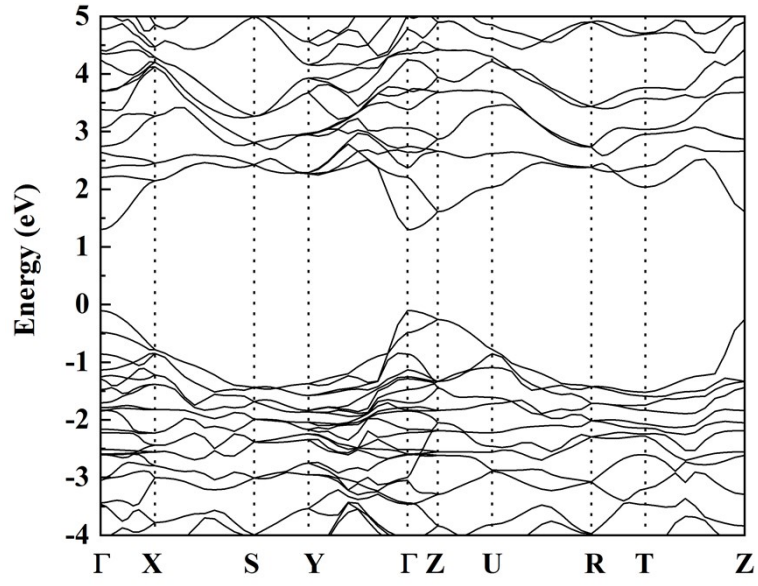


FIG. S1: Band structures of Ca₃PN ppPv-*Pnma* at 30 GPa (Using HSE06 method).

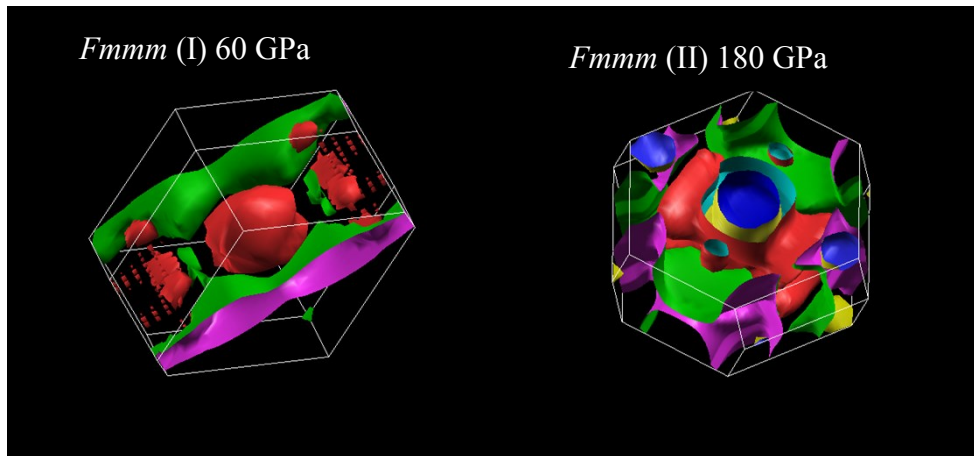


FIG. S2: The 3D Fermi surface of two Ca_3PN $Fm\bar{3}m$ phases.

Table S1. The relaxed lattice parameters and reduced atomic coordinates of Ca_3PN (Pv-Pnma , ppPv-Pnma , $Fmmm$ (I), $Fmmm$ (II) and ppPv-Cmcm).

	<i>Atoms</i>	<i>Wykc.</i>	<i>Coordinates</i>		
			<i>x</i>	<i>y</i>	<i>z</i>
<i>Pv-Pnma</i> (0 GPa)	$a=6.7564\text{\AA}, b=9.4482\text{\AA}, c=6.6398\text{\AA}$				
	Ca1	8d	0.29296	0.5368	0.70673
	P	4c	0.95832	0.25	0.00863
	Ca2	4c	0.52078	0.25	0.93027
	N	4b	0	0	0.5
<i>ppPv-Pnma</i> (30 GPa)	$a=6.7884\text{\AA}, b=3.7104\text{\AA}, c=12.2239\text{\AA}$				
	P	4c	0.5867	0.25	0.83287
	N	4c	0.35446	0.25	0.432
	Ca1	4c	0.32523	0.25	0.00539
	Ca2	4c	0.97332	0.25	0.89069
	Ca3	4c	0.68796	0.25	0.22055
<i>Fmmm</i> (I) (60 GPa)	$a=5.6477\text{\AA}, b=12.0310\text{\AA}, c=7.2197\text{\AA}$				
	P	8g	0.19823	0	0
	N	8f	0.75	0.75	0.75
	Ca1	16m	0.5	0.89431	0.79475
	Ca2	8h	0.5	0.70833	0
<i>Fmmm</i> (II) (180 GPa)	$a=3.8106\text{\AA}, b=14.0863\text{\AA}, c=6.5346\text{\AA}$				
	P	8h	0	0.92045	0
	N	8h	0	0.19696	0
	Ca1	8i	0	0	0.33463
	Ca2	16m	0.5	0.1727	0.83436
<i>ppPv-Cmcm</i> (90 GPa)	$a=3.37500\text{\AA}, b=13.34940\text{\AA}, c=4.85650\text{\AA}$				
	P	4c	-0.5	0.50473	-0.75
	N	4c	0	0.20438	-0.25
	Ca1	4c	0	-0.20532	-0.25
	Ca2	8f	0	0.60934	-0.01703

Table S2. Formation enthalpies (eV/f.u.) of Ca₃PN at different pressures.

	H_{Ca_3PN}	H_{CaP}	H_{Ca_2N}	ΔH
Pv (0 GPa)	-24.7973	-9.5229	-14.4676	-0.8068
ppPv (30 GPa)	-8.0547	-1.9108	-3.8303	-2.3136
<i>Fmmm</i> (I) (60 GPa)	4.8454	4.1933	2.6900	-2.0379
<i>Fmmm</i> (II) (180 GPa)	43.7269	20.3332	25.6861	-2.2924

Table S3. The phonon frequencies (cm^{-1}) of four phases in Ca_3PN .

Mode	Pv- <i>Pnma</i> (0GPa)	ppPv- <i>Pnma</i> (30GPa)	<i>Fmmm(I)</i> (60GPa)	<i>Fmmm(II)</i> (180GPa)
$A_g(\text{R})$	75.7	97.8	214.0	461.3
	97.3	168.3	323.5	565.0
	139.0	179.1	399.9	585.0
	181.2	241.1	532.6	630.1
	193.7	276.8		1009.7
	213.2	327.6		
	225.6	334.9		
		376.7		
	441.7			
	572.4			
$B_{1g}(\text{R})$	92.0	132.2	206.8	215.3
	136.1	217.5	267.1	495.6
	190.3	236.3	335.8	727.3
	210.9	315.4	414.8	
	289.7	502.2		
$B_{2g}(\text{R})$	88.7	139.7	261.3	552.0
	137.0	193.2	450.8	596.3
	175.7	224.1	556.8	
	206.3	239.6		
	225.5	294.0		
	264.8	328.6		
	313.6	367.5		
		394.3		
	451.0			
	584.6			
$B_{3g}(\text{R})$	137.9	213.5	181.4	216.0
	195.7	225.5	260.9	284.5
	196.7	230.6	366.6	381.3
	220.2	297.0	699.8	516.6
	337.8	500.7		682.9
A_u	87.2	121.5	331.3	597.9
	120.1	202.2		
	184.6	237.3		
	205.0	286.1		
	243.3	475.5		
	326.0			
	347.0			
415.4				
B_{1u}	117.5	104.3	264.5	244.5
	136.8	186.0	367.5	303.8

	162.7	230.7	452.3	554.3
	188.3	323.0	483.2	697.3
	223.3	333.3		
	259.0	358.1		
	321.1	368.1		
	406.8	450.4		
	431.0	517.7		
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B _{2u}	95.9	180.9	306.0	440.9
	174.6	219.7	344.8	516.0
	235.8	265.9	385.1	626.5
	252.8	475.9	593.5	950.3
	322.6			
	347.4			
	415.8			
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B _{3u}	119.8	158.5	139.6	245.2
	144.4	194.0	379.5	524.3
	172.0	201.1	490.3	635.6
	186.0	224.1		
	229.0	312.3		
	251.0	360.0		
	323.8	367.2		
	409.2	428.4		
	475.8	603.2		
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Table S4. Elastic constants of Ca₃PN for the Pv-*Pnma*, ppPv-*Pnma*, *Fmmm* (I), and *Fmmm* (II) phases at different pressures.

	P	C ₁₁	C ₂₂	C ₃₃	C ₄₄	C ₅₅	C ₆₆	C ₁₂	C ₁₃	C ₂₃
<i>Pv-Pnma</i>	0	101	127	110	45	43	49	32	41	38
	5	121	159	126	49	52	53	39	56	50
	10	139	185	141	53	59	55	46	70	62
	15	157	206	153	55	64	57	54	82	76
ppPv-<i>Pnma</i>	20	146	185	182	78	62	76	94	64	80
	25	155	197	194	83	66	83	107	73	92
	30	161	209	204	88	69	90	120	83	103
	35	166	220	212	93	72	97	131	94	115
	40	168	231	219	98	74	104	142	106	126
<i>Fmmm</i>(I)	50	391	288	281	111	111	113	101	100	134
	60	429	319	303	119	130	128	117	121	149
	70	467	351	324	126	148	143	132	141	162
	80	506	384	350	133	166	158	146	158	178
	90	542	416	375	140	183	172	161	177	194
	100	576	449	384	147	199	186	176	202	203
	110	614	481	411	154	215	199	191	215	218
	120	648	515	458	163	229	212	205	225	236
	130	680	546	495	171	243	224	220	236	252
	140	708	577	518	179	257	236	235	256	263
	150	738	607	554	188	270	248	250	269	277
160	766	637	589	196	283	259	264	281	291	
<i>Fmmm</i>(II)	170	869	749	902	236	198	250	178	342	224
	180	909	778	940	245	210	258	185	357	236
	190	947	807	978	253	221	265	191	373	249
	200	985	836	1015	261	232	272	199	389	259

Table S5. The Voigt bulk modulus, Reuss bulk modulus, Voigt shear modulus, Reuss shear modulus of Ca_3PN for the Pv-Pnma , ppPv-Pnma , Fmmm (I) , and Fmmm (II) phases at different pressures.

	P	B_v	B_r	G_v	G_r
<i>Pv-Pnma</i>	0	62.1494	61.7592	42.4223	41.5620
	5	77.3088	76.7236	48.2357	46.6659
	10	91.2639	90.5443	52.4773	50.1739
	15	104.3417	103.5476	55.4627	52.5131
<i>ppPv-Pnma</i>	20	109.9163	107.5463	61.4783	56.4253
	25	121.0662	118.1087	64.7465	57.7387
	30	131.7292	127.9249	67.4405	58.1206
	35	141.9838	136.9190	69.6076	57.4839
	40	151.8646	144.9596	71.3392	55.7940
<i>Fmmm(I)</i>	50	181.3434	179.8474	108.4978	104.5642
	60	202.8199	200.6762	119.6539	114.9968
	70	223.6152	220.7601	130.4497	124.9768
	80	244.9733	241.7759	141.7971	135.2059
	90	266.1887	262.5736	152.3798	144.5767
	100	285.6484	280.1527	161.4398	152.0826
	110	305.9510	300.1304	172.3914	162.2592
	120	328.2302	323.9471	184.4846	175.0176
	130	348.5584	344.7922	195.3277	185.9155
	140	367.9347	363.7754	204.4204	194.5618
	150	387.7927	384.1335	214.6286	204.9246
<i>Fmmm(II)</i>	160	407.2477	404.0118	224.6521	215.1065
	170	445.3408	435.7197	255.4323	248.2075
	180	464.8285	454.4205	265.8257	258.5963
	190	484.1467	472.9512	275.8415	268.5688
	200	503.2239	491.3199	285.5620	278.2219

Table S6. The Bulk modulus, Shear modulus, Young's modulus, Poisson's ratio of Ca₃PN for the Pv-*Pnma*, ppPv-*Pnma*, *Fmmm* (I), and *Fmmm* (II) phases at different pressures.

	P	B	G	B/G	Y	σ
Pv-<i>Pnma</i>	0	61.9543	41.9921	1.4754	102.7598	0.2236
	5	77.0162	47.4508	1.6231	118.0984	0.2444
	10	90.9041	51.3256	1.7711	129.5878	0.2624
	15	103.9446	53.9879	1.9253	138.0612	0.2786
ppPv-<i>Pnma</i>	20	108.7313	58.9518	1.8444	149.7852	0.2704
	25	119.5875	61.2426	1.9527	156.9378	0.2813
	30	129.8270	62.7805	2.0680	162.1970	0.2918
	35	139.4514	63.5458	2.1945	165.4989	0.3022
	40	148.4121	63.5666	2.3347	166.8750	0.3126
<i>Fmmm</i>(I)	50	180.5954	106.5310	1.6952	267.0777	0.2535
	60	201.7481	117.3254	1.7196	294.8249	0.2564
	70	222.1877	127.7133	1.7397	321.5340	0.2588
	80	243.3746	138.5015	1.7572	349.2527	0.2608
	90	264.3812	148.4782	1.7806	375.1970	0.2635
	100	282.9006	156.7612	1.8047	396.9619	0.2661
	110	303.0407	167.3253	1.8111	423.9477	0.2668
	120	326.0887	179.7511	1.8141	455.5487	0.2672
	130	346.6753	190.6216	1.8187	483.2857	0.2677
	140	365.8550	199.4911	1.8339	506.4264	0.2693
	150	385.9631	209.7766	1.8399	532.8013	0.2699
160	405.6297	219.8793	1.8448	558.6887	0.2704	
<i>Fmmm</i>(II)	170	440.5303	251.8199	1.7494	634.5505	0.2599
	180	459.6245	262.2110	1.7529	660.9455	0.2603
	190	478.5489	272.2052	1.7580	686.4596	0.2609
	200	497.2719	281.8920	1.7641	711.2742	0.2616

Table S7. The calculated bond number n , bond length d , bond volume V_b , Mulliken overlap population P and Vickers hardness (GPa) H of Ca_3PN for the $Pv\text{-}Pnma$, $ppPv\text{-}Pnma$, $Fmmm$ (I), and $Fmmm$ (II) phases at different pressures.

	n	$Bond$	d	V_b	P	H_n	H
$Pv\text{-}Pnma$ (0 GPa)	4	Ca-N	2.41	4.56	0.25	14.78	6.02
	4	Ca-N	2.41	4.56	0.25	14.78	
	4	Ca-P	2.95	8.30	0.30	6.52	
	4	Ca-P	3.00	8.79	0.27	5.33	
	8	2Ca-N	2.42	4.62	0.24	13.84	
	8	2Ca-N	2.43	4.69	0.24	13.53	
	8	2Ca-P	2.94	8.22	0.23	5.09	
	8	2Ca-P	3.24	11.08	0.14	1.88	
	8	2Ca-P	3.26	11.27	0.14	1.83	
$ppPv\text{-}Pnma$ (30 GPa)	4	Ca-N	2.18	4.58	0.32	18.76	6.70
	4	Ca-N	2.25	5.03	0.49	24.54	
	4	Ca-N	2.31	5.46	0.18	7.86	
	4	Ca-N	2.39	6.06	0.42	15.41	
	4	Ca-P	2.71	8.79	0.33	6.52	
	4	Ca-P	2.72	8.87	0.17	3.31	
	4	Ca-P	2.76	9.25	0.23	4.18	
	4	Ca-P	2.77	9.37	0.34	6.04	
	4	Ca-P	2.78	9.45	0.34	5.96	
	4	Ca-P	2.84	10.11	0.14	2.19	
	$Fmmm$(I) (60 GPa)	1	P-P	2.24	4.34	0.25	
8		Ca-N	2.26	4.47	0.17	10.37	
4		Ca-N	2.35	4.99	0.31	15.73	
8		Ca-P	2.59	6.73	0.17	5.24	
1		N-N	2.82	8.71	0.11	2.21	
$Fmmm$(II) (180 GPa)	2	N-P	1.65	2.99	0.18	21.48	5.71
	4	Ca-N	2.21	7.15	0.23	6.42	
	1	N-N	2.42	9.38	0.22	3.90	
	4	Ca-P	2.55	10.94	0.21	2.88	