Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information of

Pressure-induced Reconstructive Phase Transitions, Polarization with Metallicity, and Enhanced Hardness in Antiperovskite $MgCNi_3$

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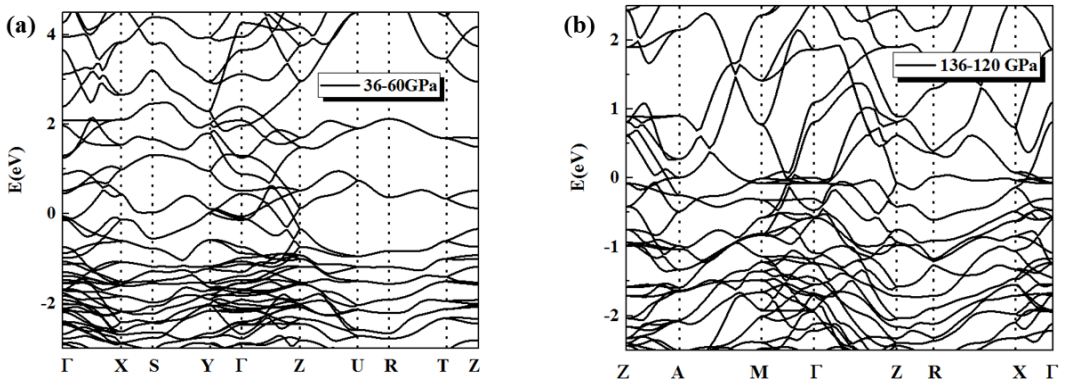
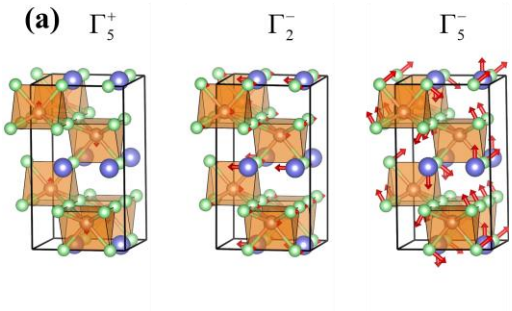


Figure S1. The energy band structures of two novel phases, i.e., (a) *Cmc*2_1 phase at 60 GPa and (b) *P*4_2/*mnm* phase at 120 GPa. This figure indicates the two novel phases both exhibit metallicity.



(b)

Mode	Amplitude (Å/atom)	Energy (eV/atom)
Γ_5^+	0.002	+0.005
Γ_2^-	0.037	−0.128
Γ_5^-	0.078	−0.356

Figure S2. Schematization of the three distortions modes, i.e., Γ_5^+, Γ_2^-, and Γ_5^- modes, in the *Cmc*2_1 phase of $MgCNi_3$ with respect to its high-symmetry *P*6_3/*mmc* state, as well as their amplitudes and the changes of energy with respect to *P*6_3/*mmc* state. The red arrows represent the atomic displacements of the different distortion modes. Note that due to the rather small amplitude of Γ_5^+ mode (< 0.002 Å/atom), we will only consider the two main distortion in the main text --- Γ_2^-, and Γ_5^- modes.

Table S1. The relaxed lattice parameters and reduced atomic coordinates of $MgCNi_3$ (*Pm*-3*m*, *Cmc*2_1 and *P*4_2/*mnm*).

	Atoms	*Wykc.*	*Coordinates*		
			x	*y*	*z*
		*a=b=c=3.7647*Å			
Pm-3*m*	Mg	1a	0	0	0
(0 GPa)	C	1a	0.5	0.5	0.5
	Ni	3a	0	0.5	0.5
		*a= 4.5372*Å, *b=8.2622*Å, *c=4.5248*Å			
Cmc2_1	Mg	4a	0.5867	0.25	0.83287
(60 GPa)	C	4a	0.35446	0.25	0.432
	Ni1	4a	0.32523	0.25	0.00539
	Ni2	8b	0.68796	0.25	0.22055
		*a=b=6.8991*Å, *c=3.1106*Å			
P4_2/*mnm*	Mg	4g	0.1406	0.1406	0.5
(120 GPa)	C	4g	0.57256	0.57256	0.5
	Ni1	8i	0.83775	0.51489	0.5
	Ni2	4f	0.68446	0.68446	0

Table S2. Elastic constants of $MgCNi_3$ different phases at different pressures. For the cubic phase with three independent terms of C_{11}, C_{44} and C_{12}; its mechanical stability criterion is[1], $C_{ii} > 0 \quad (i = 1,4)$, $C_{11} > |C_{12}|$, $(C_{11} + 2C_{12}) > 0$. After careful inspection, the elastic constants of three phases we calculated meet the above requirements.

	P	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
	0	375			53			117		
Pm-3*m*	10	440			59			134		
	20	501			64			151		
	30	506	442	358	152	98	130	195	230	289
	40	543	483	414	164	101	135	221	261	307
	50	582	521	463	176	105	142	245	285	328
Cmc2_1	60	621	558	509	187	110	148	270	309	349
	70	659	593	554	198	113	153	295	331	368
	80	698	629	603	209	117	160	317	352	388
	90	734	663	645	219	120	165	341	373	408
	100	823		648	304	304	133	263	423	
	110	864		680	319	319	140	280	447	
P4_2*/mnm*	120	904		709	334	334	145	296	470	
	130	943		737	348	348	151	313	493	
	140	981		765	362	362	156	329	516	

[1]Wu Z, Zhao E, Xiang H, *et al*. ***Phys. Rev. B***, 2007, 76(5): 054115.

Table S3. The Bulk modulus *B* (GPa), Shear modulus *G* (GPa), Young's modulus (GPa), Poisson's ratio of $MgCNi_3$ different phases at different pressures P (GPa).

	P	*B*	*G*	*B/G*	*Y*	σ
Pm-3*m*	0	202.884	76.438	2.654	203.729	0.333
	10	236.267	87.323	2.706	233.234	0.335
	20	267.701	97.489	2.746	260.807	0.338
Cmc2_1	30	302.906	106.189	2.853	285.235	0.343
	40	335.015	116.735	2.870	313.762	0.344
	50	364.841	126.026	2.895	339.041	0.345
	60	393.546	134.513	2.926	362.266	0.347
	70	421.432	142.417	2.959	383.996	0.348
	80	449.396	150.671	2.983	406.575	0.349
	90	476.143	157.670	3.020	425.989	0.351
P4_2/*mnm*	100	432.498	197.562	2.189	514.366	0.302
	110	459.260	207.619	2.212	541.289	0.304
	120	484.595	216.376	2.240	565.031	0.306
	130	522.905	227.203	2.301	595.378	0.310
	140	552.144	236.218	2.337	620.209	0.313

Table S4. The calculated bond number *n*, bond length *d*, Mulliken overlap population *P*, bond volume V_b, and Vickers hardness (GPa) *H* of $MgCNi_3$ different phases at different pressures.

	n	*Bond*	*d*	*P*	V_b	H_n	*H*
Pm-3*m*	3	C-Ni	1.88	0.73	6.51	23.80	9.895
(0 GPa)	1	C-Mg	3.26	0.34	33.83	0.71	
	2	C-Ni	1.83	0.34	3.47	31.61	13.807
	4	C-Ni	1.84	0.28	3.51	25.54	
Cmc2_1	4	C-Ni	1.85	0.27	3.56	24.09	
(60 GPa)	2	C-Ni	1.85	0.32	3.57	28.39	
	2	C-Mg	2.46	0.10	8.44	2.12	
	2	C-Mg	2.83	0.18	12.79	1.90	
	2	C-C	1.42	0.98	0.89	874.09	18.813
P4_2/*mnm*	8	C-Ni	1.87	0.22	2.07	48.52	
(120 GPa)	4	C-Ni	1.90	1.04	2.16	213.00	
	4	C-Mg	2.80	0.07	6.90	2.07	
	8	C-Ni	2.89	0.15	7.64	3.75	
	4	C-Ni	2.95	0.37	8.09	8.39	