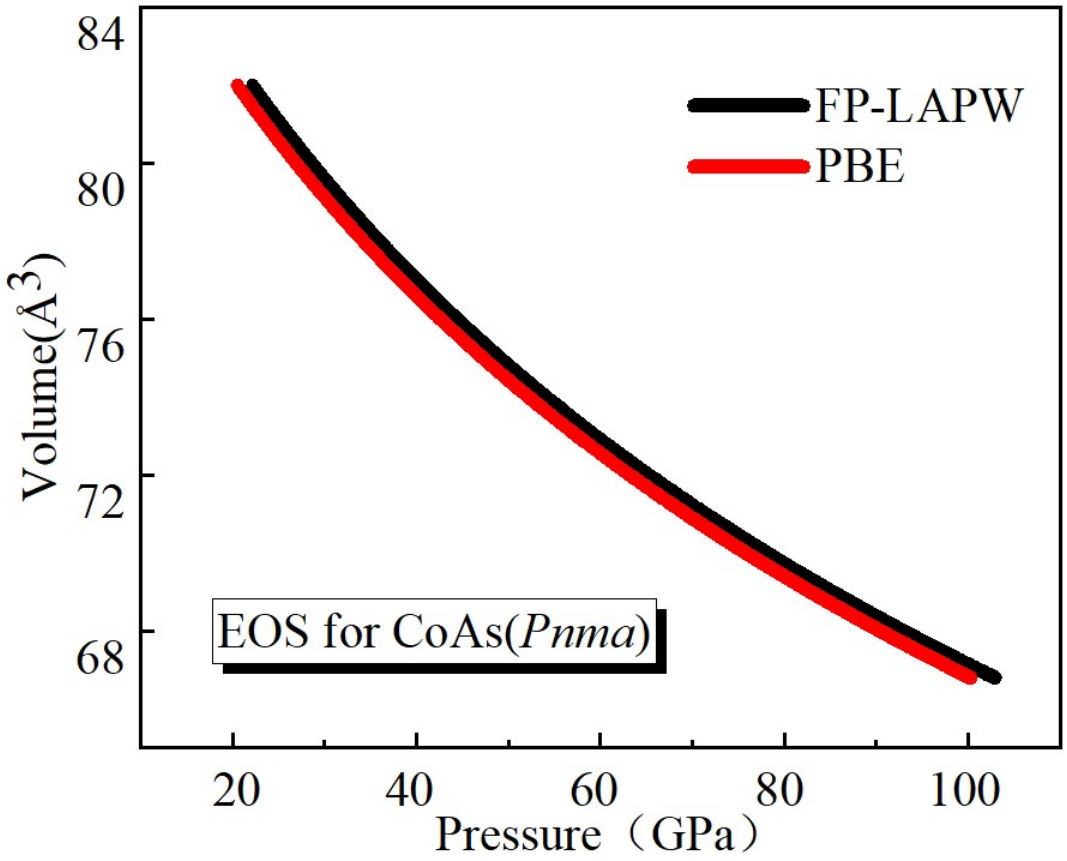
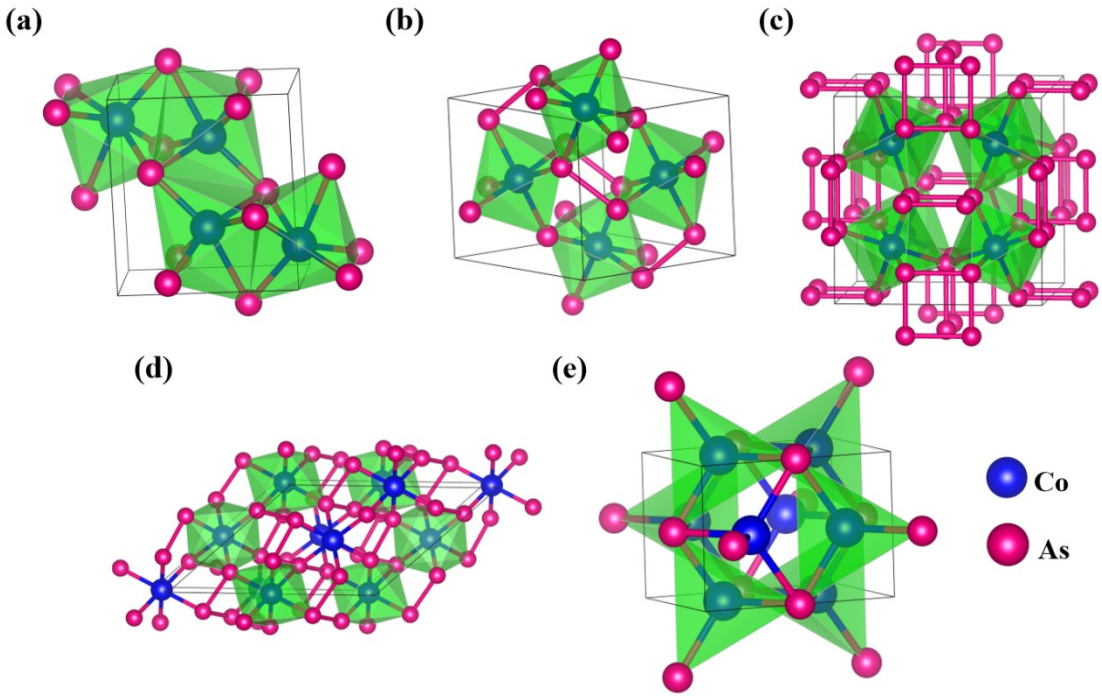
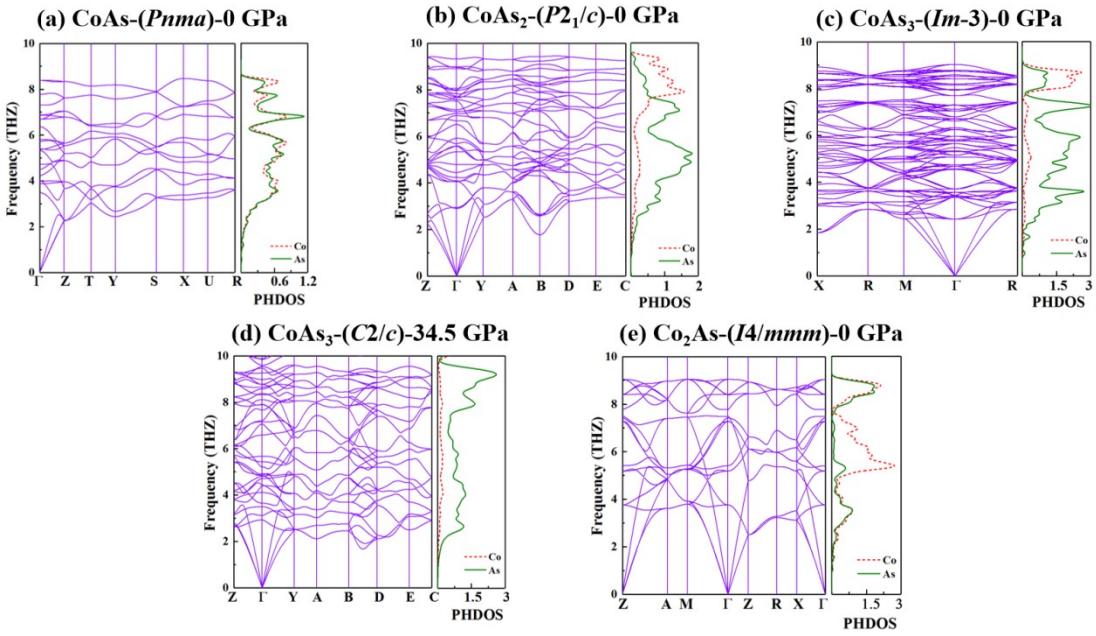
Electronic Supplementary Material (ESI) for RSC Advances.



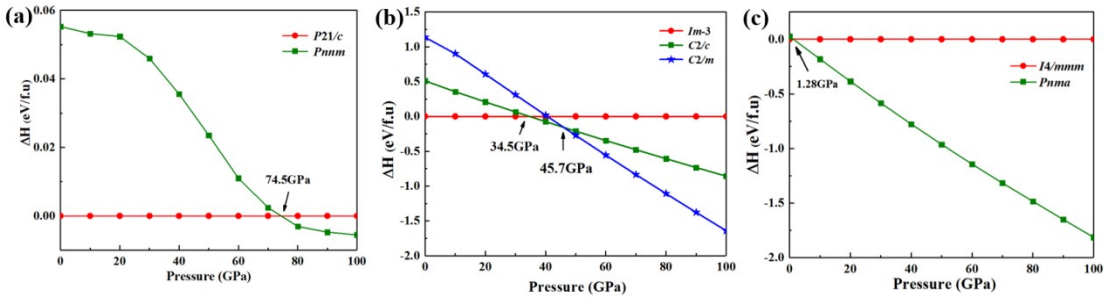
Supplemental Figure 0. Volumes as a function of pressures for *Pnma*-CoAs calculated by using the generalized gradient approximation Perdew-Burke-Ernzerhof in VASP calculations and full-potential in WIEN2K calculations. The two calculations gave identical results. The results suggest the generalized gradient approximation Perdew-Burke-Ernzerhof is reliable in the pressure range of current work.



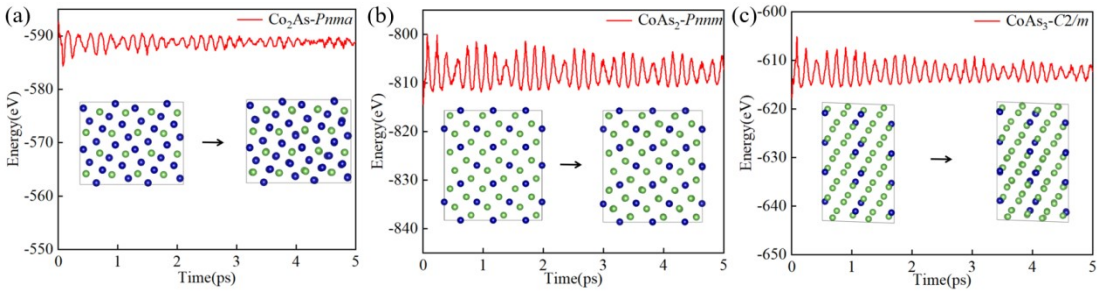
Supplemental Figure 1. Structures of predicted stable Co-As system for (a) *Pnma* structure of CoAs; (b) $P2_1/c$ structure of $CoAs_2$; (c) *Im*-3 structure of $CoAs_3$; (d) $C2/c$ structure of $CoAs_3$; and (e) $I4/mmm$ structure of Co_2As. The blue and pink spheres are Co atom and As atom, respectively.



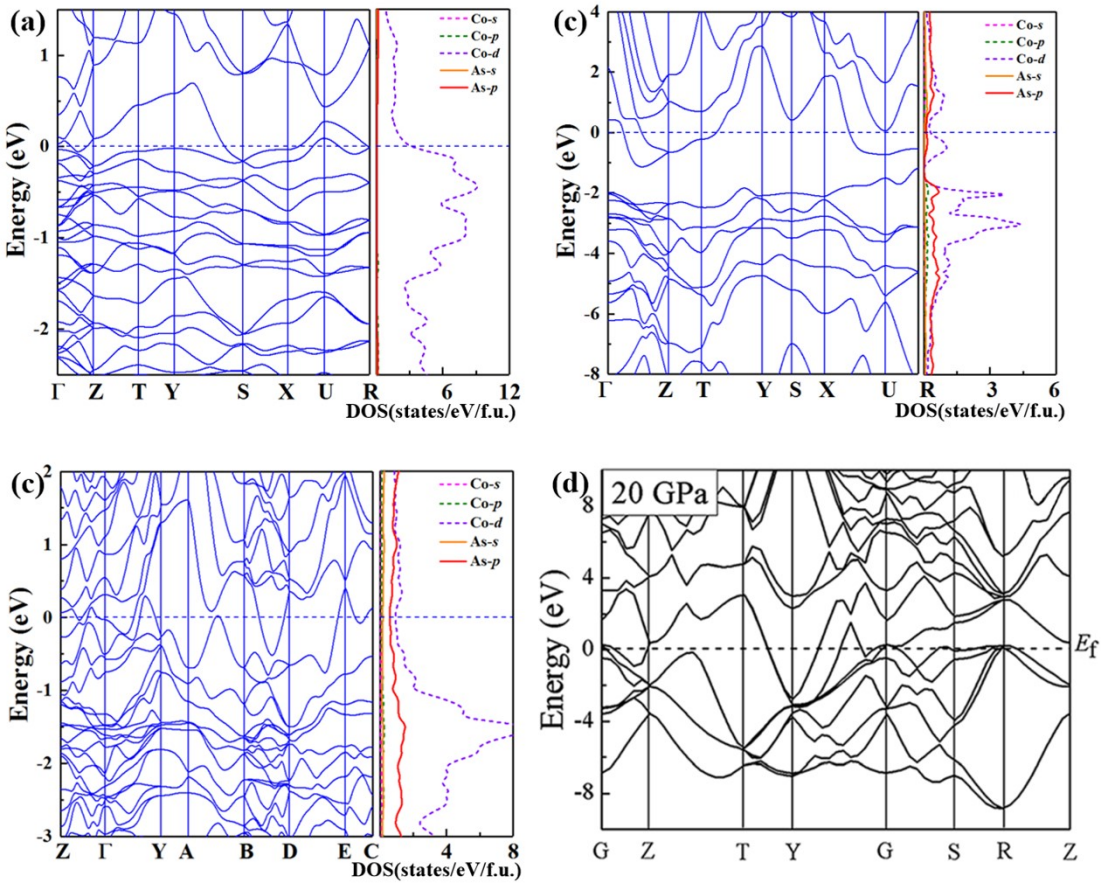
Supplemental Figure 2. Phonon dispersion relations and PHDOS projected on Co atoms and As atoms of structures with stable existence predicted in the Co-As system:(a) CoAs-*Pnma* at 0 GPa; (b) $CoAs_2$-$P2_1/c$ at 0 GPa; (c) $CoAs_3$-*Im*-3 at 0 GPa; (d) $CoAs_3$-*C*2/*c* at 34.5 GPa; and (e) Co_2As-*I*4/*mmm* at 0 GPa.



Supplemental Figure 3. Calculated enthalpy difference as a function of pressure relative to (a) $CoAs_2$,(b) $CoAs_3$ and (c) Co_2As.



Supplemental Figure 4. Calculated the ab initio molecular dynamics at 300K for (a) Co_2As-*Pnma*, (b) $CoAs_2$-*Pnnm*, and (c) $CoAs_3$-*C*2/*m*, respectively.



Supplemental Figure 5. Electronic band structure and the projected electronic DOS on Co atoms and As atoms for (a) Co_2As-*Pnma* at 1.28 GPa; (b) $CoAs_2$-*Pnnm* at 74.5 GPa; (c) $CoAs_3$-*C*2/*m* at 45.7 GPa. And figure (d) shows the electronic band structure of GaAs at 20GPa.[1] Note that Zero energy is at the Fermi level.

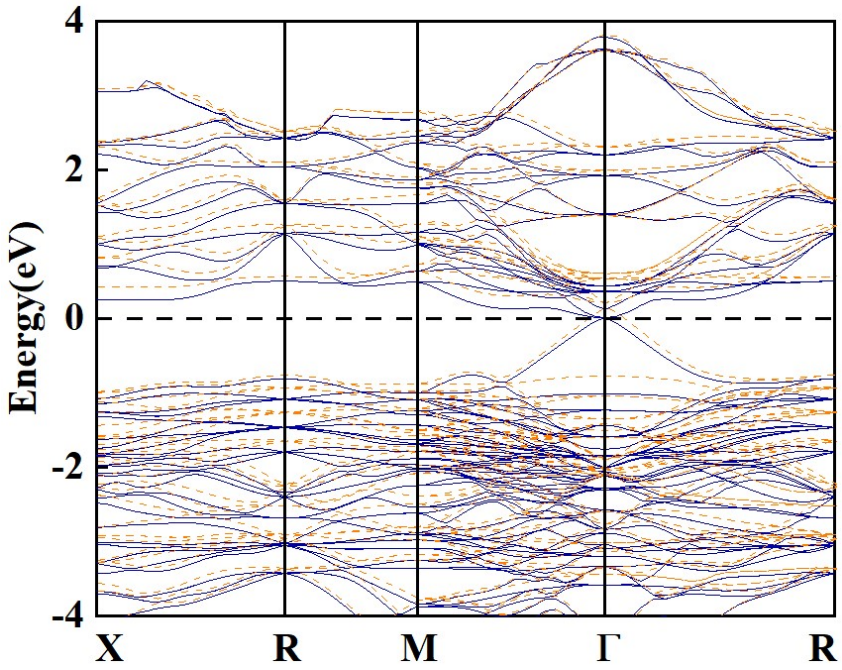
Supplemental Table 1. Strctural information of the predicted stable compounds.

	Phase	Lattice Parameters (Å)		Atoms	Wyckoff position	x	y	z
	Pnma	a = 5.350	α = 90.0°	Co1	4*c*	1.000	0.750	0.198
CoAs	0 GPa	b = 3.499	β = 90.0°	As1	4*c*	0.702	0.250	0.089
		c = 5.883	γ = 90.0°					
	*P*21/*c*	a =5.938	α = 90.0°	Co1	4*e*	0.272	0.001	0.286
$CoAs_2$	0 GPa	b = 5.891	β = 116.0°	As1	4*e*	0.153	0.634	0.368
		c = 5.994	γ = 90.0°	As2	4*e*	0.343	0.136	0.675
	Im-3	a = 8.335	α = 90.0°	Co1	8*c*	0.750	0.750	0.750
	0 GPa	b = 8.335	β = 90.0°	As1	24*g*	0.000	0.341	0.152
		c =8.335	γ = 90.0°					
$CoAs_3$	*C*2/*c*	a = 9.781	α = 90.0°	Co1	4*b*	0.000	0.500	0.000
	34.5 GPa	b = 4.532	β = 137.9°	As1	8*f*	0.300	1.342	-0.315
		c = 7.664	γ = 90.0°	As2	4*e*	-0.500	1.264	0.250
	*I*4/*mmm*	a = 3.829	α = 90.0°	Co1	4*d*	0.500	0.000	0.750
Co_2As	0 GPa	b = 3.829	β = 90.0°	As1	2*b*	0.000	0.000	0.500
		c = 5.420	γ = 90.0°					

We used rotationally invariant DFT+U version proposed by Dudarev et al.[2] In this method, the parameters U and J represented on-site Coulomb interaction energy and exchange energy, respectively. The parameters U and J were not used separately, only their difference U-J was meaningful. we use (U-J)=1.8 eV for Co, where the exchange energy parameter is set to the typical value of J=1 eV.[3] Moreover, by comparing with the case without U, the result proved that U had less impact on the Co-As system. Thus, we ignore the effect of the U value for the Co-As system.

Supplemental Table 2. Calculated lattice parameter a_0 (Å), atomic volume V (Å^3), the magnetic moments M (μB), and the bandgap (eV) for CoP_3-*Im*-3 at 0 GPa by GGA and GGA+U, respectively, together with experimental data.

Phase	Method	a_0(Å)	V(Å^3)	M (μB)	Bandgap(eV)
$CoAs_3$-*Im*-3-our calulation	GGA	8.271	565.81	0	none
	GGA+U	8.260	563.56	0	none
Reference	exp.[4]	8.208	552.98	0	none



Supplemental Figure 6. Calculated the electronic band structure for CoP_3-*Im*-3 at 0 GPa by GGA and GGA+U, respectively. The dashed (orange) and solid (blue) lines in the band structures represent the results obtained using the GGA and GGA+U, respectively.

[1] J. Wang, B. Wu, G. Zhang, L. Tian, G. Gu, C. Gao. *Rsc. Adv.* 2016, **6(12)**, 10144-10149.
[2] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, *Phys. Rev. B.* 1998, **57**, 1505.
[3] Y. S. Mohammed, Y. Yan, H. Wang, K. Li, X. Du, *J. Magn. Magn. Mater.*, 2010, **322(6)**, 653-657.
[4] J. Ackermann, A. Wold, *J. Phys. Chem. Solid.*, 1977, **38(9)**, 1013-1016.