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

Supplementary Materials: Towards the ionic limit of two-dimensional materials: monolayer alkaline earth and transition metal halides

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We performed full phonon dispersion calculations as one of a series of examinations for structural stabilities. For some of the investigated materials, small imaginary frequencies were found in limited regions near Γ. With a most stringent criterion, we dismissed these materials in the main text. But it should be noted that, as discussed in details by Ataca *et al.* in Ref. [1], the phonon dispersion calculations require very high accuracy, and thus the obtained structural instability might arise from the numerical artifacts. Visible imaginary frequencies were found in Ref. [1] for several predicted materials therein, such as H-structures: ScS_2, $ScTe_2$, VO_2, FeO_2, $FeTe_2$, $CoTe_2$, $NbSe_2$, and T-structures: ScO_2, $ScTe_2$, $TiTe_2$, NiS_2, $NiSe_2$. Some of these materials can still very likely be fabricated due to that only small imaginary phonon frequencies in rather small regions were found, and sizable cohesive/formation energies were obtained via first-principles calculations. Therefore we show the phonon dispersions of these materials here in Fig. 1, and summarized their properties, with other predicted materials discussed in the main text, in Table I.

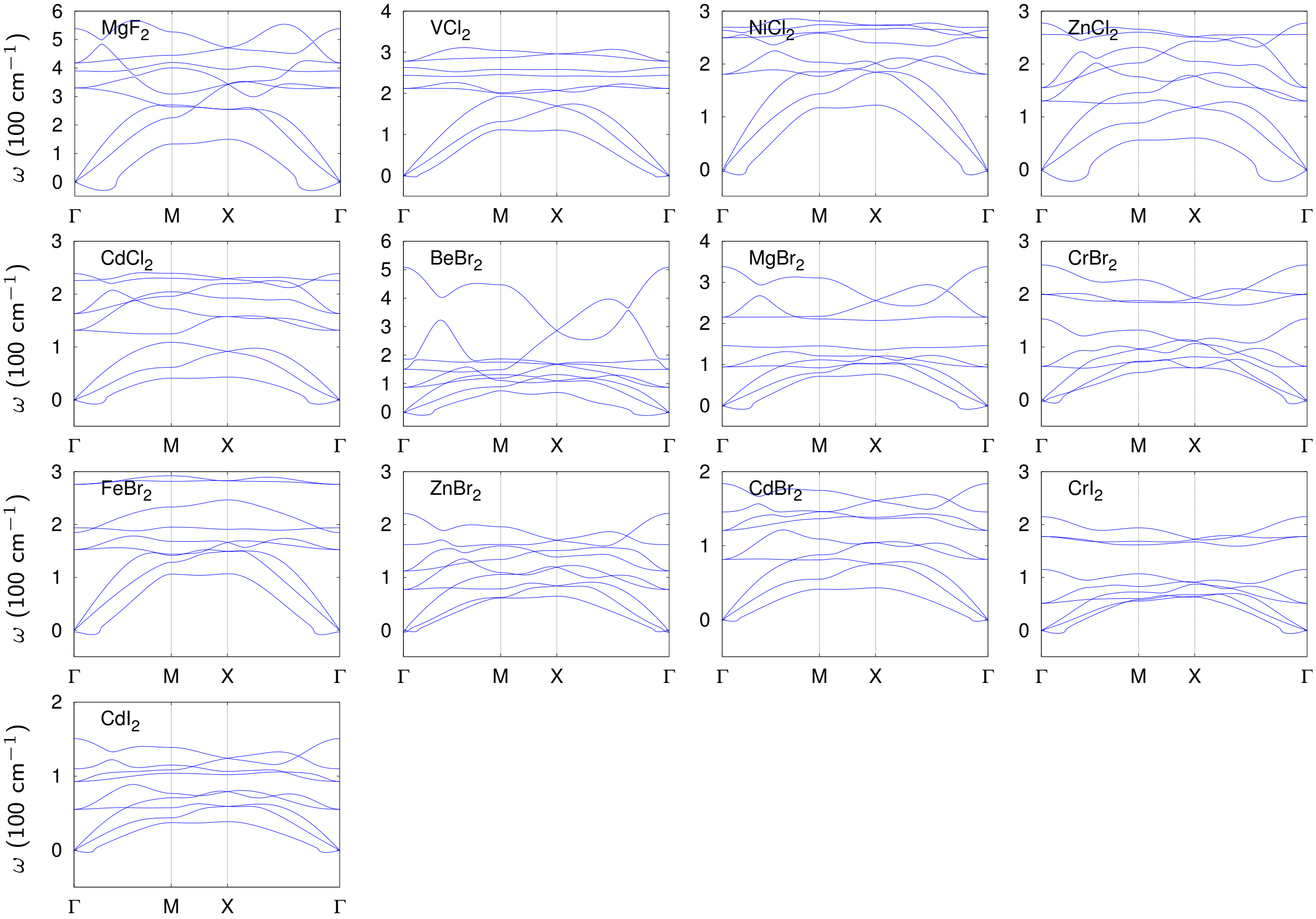

FIG. 1. Phonon dispersions for the investigated materials with small imaginary phonon frequencies near Γ.

Their band structures calculated with the LDA functional are presented in Fig. 2. All the general trends that we discussed in main text are valid for these materials as well. We also calculated band structures with the PBE functional, which can be compared with the LDA results in the main text. Most of the features agree well with the LDA results except a few materials. For example, ZnF_2 has an indirect gap with LDA, but direct gap with PBE, meanwhile $MgCl_2$ has an direct gap with LDA, but indirect gap with PBE. A more dramatic exception is NiI_2, which is metal under LDA but insulator under PBE.

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[1] C. Ataca, H. Şahin, and S. Ciraci, J. Phys. Chem. C **116**, 8983 (2012).

	a (Å)	d_{M-X} (Å)	d_{X-X} (Å)	θ (deg)	E_c (eV)	E_f (eV)	E_g (eV)	μ (μ_B)	ρ_M (e^-)	ρ_X (e^-)	layered bulk
BeF_2	2.56(2.62)	1.72	2.31	84.19	17.59	9.75	9.67^i (9.25^i)	0.00	-1.53	0.75	×
MgF_2	3.04(3.12)	1.98	2.54	79.90	16.49	10.96	7.65^i (7.35^i)	0.00	-1.46	0.73	×
CaF_2	3.53(3.62)	2.24	2.75	75.83	17.99	12.17	7.25^i (7.03^i)	0.00	-1.53	0.79	×
SrF_2	3.81(3.92)	2.39	2.89	74.28	17.51	11.88	6.75^i (6.49^i)	0.00	-1.64	0.82	×
MnF_2	3.24(3.35)	2.10	2.65	78.56	15.40	6.51	2.05^d (2.34^d)	5.00	-1.39	0.69	×
NiF_2	3.00(3.11)	1.98	2.58	81.40	14.92	4.98	0.83^i (0.99^i)	2.00	-1.26	0.63	×
ZnF_2	3.09(3.19)	2.02	2.62	80.51	12.84	7.24	4.55^i (4.46^d)	0.00	-1.35	0.68	×
CdF_2	3.46(3.57)	2.22	2.79	77.69	11.89	6.62	3.77^d (3.82^d)	0.00	-1.36	0.67	×
$BeCl_2$	3.17(3.26)	2.21	3.07	88.09	12.02	7.06	5.82^i (5.89^i)	0.00	-1.05	0.52	×
$MgCl_2$	3.56(3.67)	2.47	3.42	87.68	11.55	8.90	6.04^d (5.98^i)	0.00	-0.98	0.49	○
$SrCl_2$	4.31(4.45)	2.84	3.71	81.43	13.26	10.52	5.75^i (5.75^i)	0.00	-1.24	0.60	×
$ScCl_2$	3.45(3.58)	2.52	3.67	93.59	15.20	9.21	M (M)	0.00	-1.02	0.51	-
VCl_2	3.53(3.65)	2.42	3.30	86.17	13.86	6.28	0.93^i (1.18^i)	3.00	-0.81	0.40	-
$NiCl_2$	3.36(3.49)	2.32	3.20	87.30	11.87	4.82	4.68^i (4.72^i)	2.00	-0.85	0.42	○
$ZnCl_2$	3.47(3.60)	2.42	3.36	88.17	9.24	6.52	4.59^i (4.46^i)	0.00	-0.66	0.32	○
$CdCl_2$	3.76(3.91)	2.60	3.59	87.33	8.75	6.37	3.96^d (3.88^d)	0.00	-0.75	0.37	○
$BeBr_2$	3.42(3.51)	2.39	3.35	88.75	10.55	3.41	4.26^i (4.32^i)	0.00	-0.51	0.27	-
$MgBr_2$	3.76(3.88)	2.64	3.69	88.97	10.20	5.38	4.80^d (4.77^d)	0.00	-0.86	0.43	○
$SrBr_2$	4.44(4.61)	3.00	4.02	84.27	12.05	7.13	5.00^i (5.01^i)	0.00	-1.06	0.50	×
$ScBr_2$	3.62(3.76)	2.67	3.92	94.55	13.87	5.71	M (M)	0.00	-0.99	0.50	-
VBr_2	3.71(3.84)	2.56	3.54	87.33	12.61	2.86	0.84^i (1.08^i)	3.00	-0.63	0.32	-
$CrBr_2$	3.66(3.83)	2.58	3.62	89.31	10.51	2.00	M (M)	4.00	-0.59	0.30	○
$FeBr_2$	3.49(3.60)	2.38	3.23	85.46	11.25	1.66	0.81^i (0.82^i)	0.00	-0.10	0.02	○
$CoBr_2$	3.49(3.75)	2.40	3.31	86.98	11.18	1.60	M (0.13^i)	1.00	-0.05	0.03	○
$ZnBr_2$	3.66(3.80)	2.57	3.61	89.09	8.15	3.26	3.39^i (3.47^i)	0.00	-0.44	0.22	○
$CdBr_2$	3.91(4.07)	2.74	3.84	88.92	7.86	3.30	3.27^i (3.22^i)	0.00	-0.60	0.30	○
BeI_2	3.75(3.85)	2.63	3.69	89.07	8.95	1.20	2.41^i (2.51^i)	0.00	-0.12	0.06	-
CaI_2	4.35(4.54)	3.06	4.32	89.56	10.82	5.10	3.53^i (3.91^i)	0.00	-0.65	0.31	○
SrI_2	4.63(4.84)	3.22	4.46	87.87	10.65	5.12	3.95^i (4.33^i)	0.00	-0.84	0.40	×
ScI_2	3.90(4.05)	2.87	4.23	94.64	12.40	3.63	M (M)	0.00	-0.68	0.34	-
VI_2	3.97(4.12)	2.75	3.82	87.82	11.37	1.00	0.83^i (1.05^i)	3.00	-0.51	0.25	-
CrI_2	3.93(4.10)	2.77	3.90	89.61	9.36	0.24	M (M)	4.00	-0.14	0.07	-
FeI_2	3.74(3.86)	2.55	3.45	85.30	10.40	0.19	0.76^i (0.78^i)	0.00	0.11	-0.06	○
NiI_2	3.78(3.96)	2.64	3.67	88.36	10.08	0.24	M (2.77^i)	1.73	0.30	-0.15	○
ZnI_2	3.95(4.10)	2.78	3.93	89.69	6.92	1.42	1.86^i (2.03^i)	0.00	0.00	0.00	○
CdI_2	4.16(4.33)	2.94	4.16	89.96	6.81	1.64	2.34^i (2.48^i)	0.00	-0.15	0.08	○

TABLE I. Structural/electronic/magnetic properties of candidates for new 2D materials. The numbers in the parentheses are results of PBE. $d_{M(X)-X}$ is the distance between M(X) and X, and θ is the X-M-X bond angle. $E_c(E_f)$ are cohesive(formation) energies defined in the text. The superscripts $i(d)$ of band gap values indicate indirect(direct) gaps. Metals are denoted as "M". Acquired charge of halogens, in unit of electron charge e^-, is ρ_X. A ○ (×) is used to indicate if its layered bulk counterpart can (cannot) be found in literatures. The charge transfers of compounds involving simultaneously alkaline earth metals and halogens are significant, rendering strong ionic characters. Transition metal halides, on the other hand, exhibit versatile electronic properties.

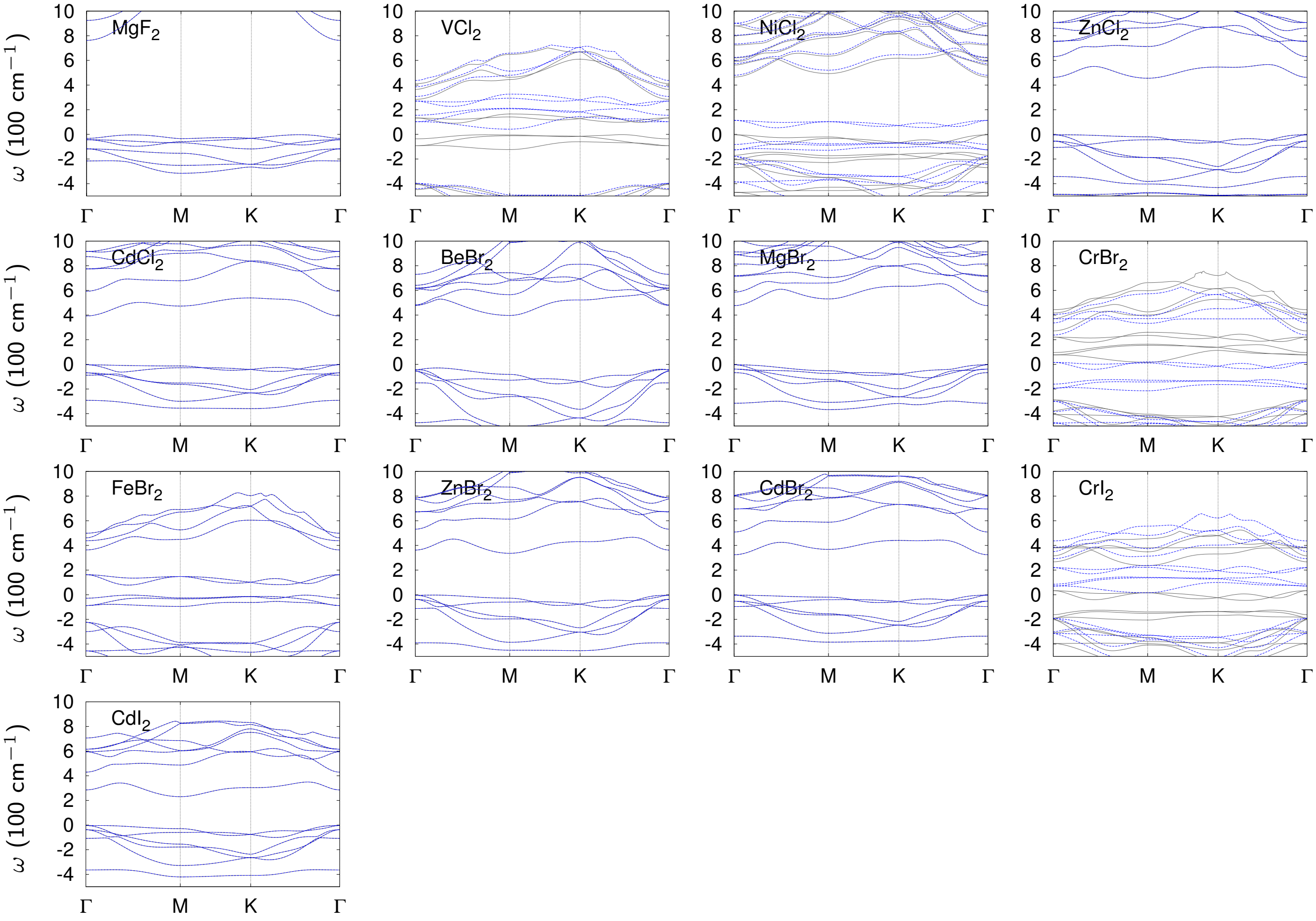

FIG. 2. Band structures using LDA for the investigated materials with small imaginary phonon frequencies near Γ.

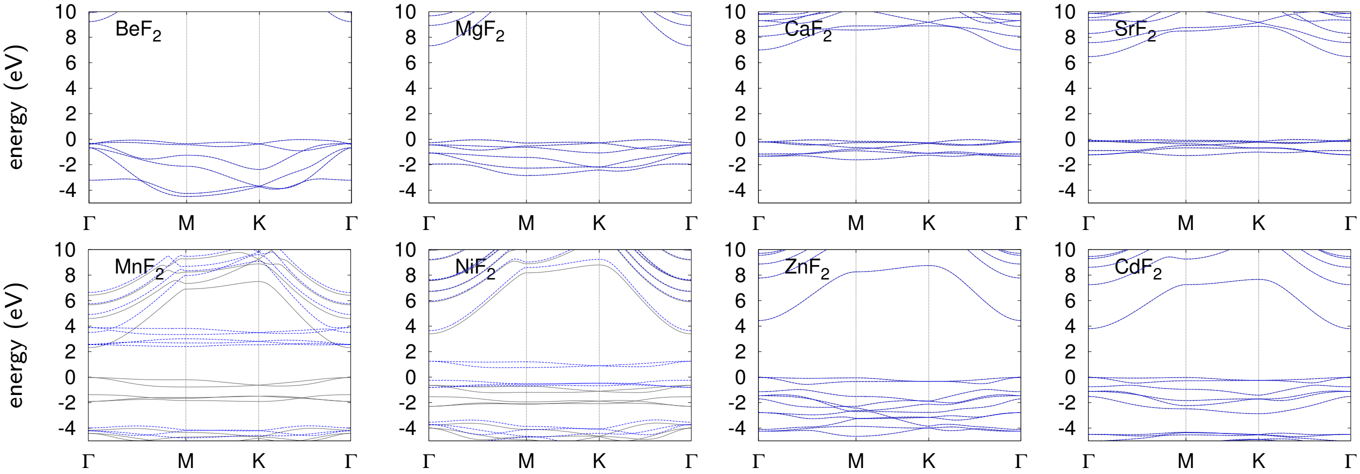

FIG. 3. Calculated band structures (PBE) for fluorides discussed in main text. The grey solid and blue dotted lines correspond to the two spin states.

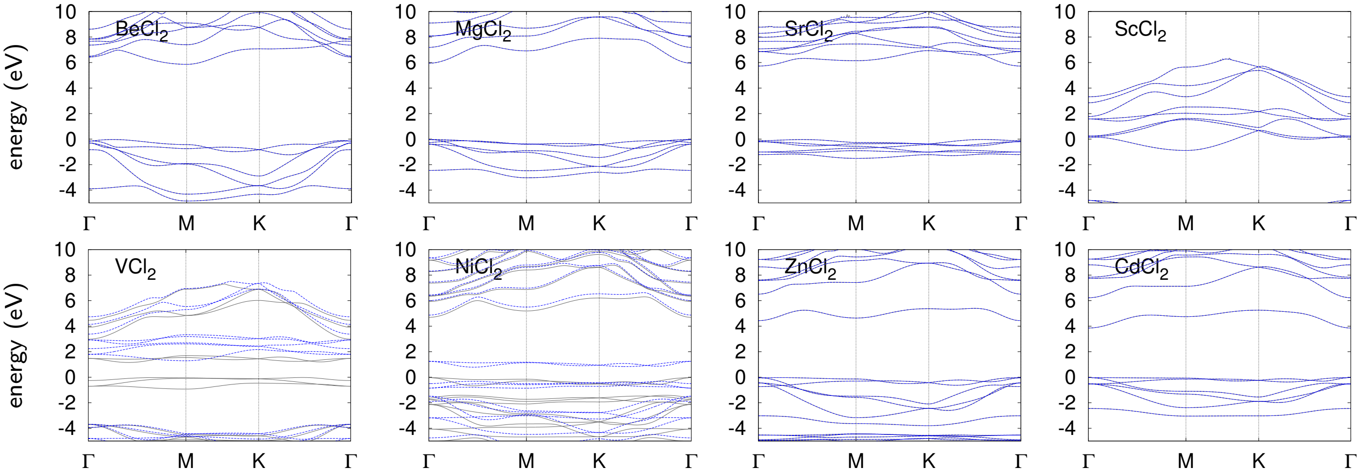

FIG. 4. Calculated band structures (PBE) for chlorides discussed in main text. The grey solid and blue dotted lines correspond to the two spin states.

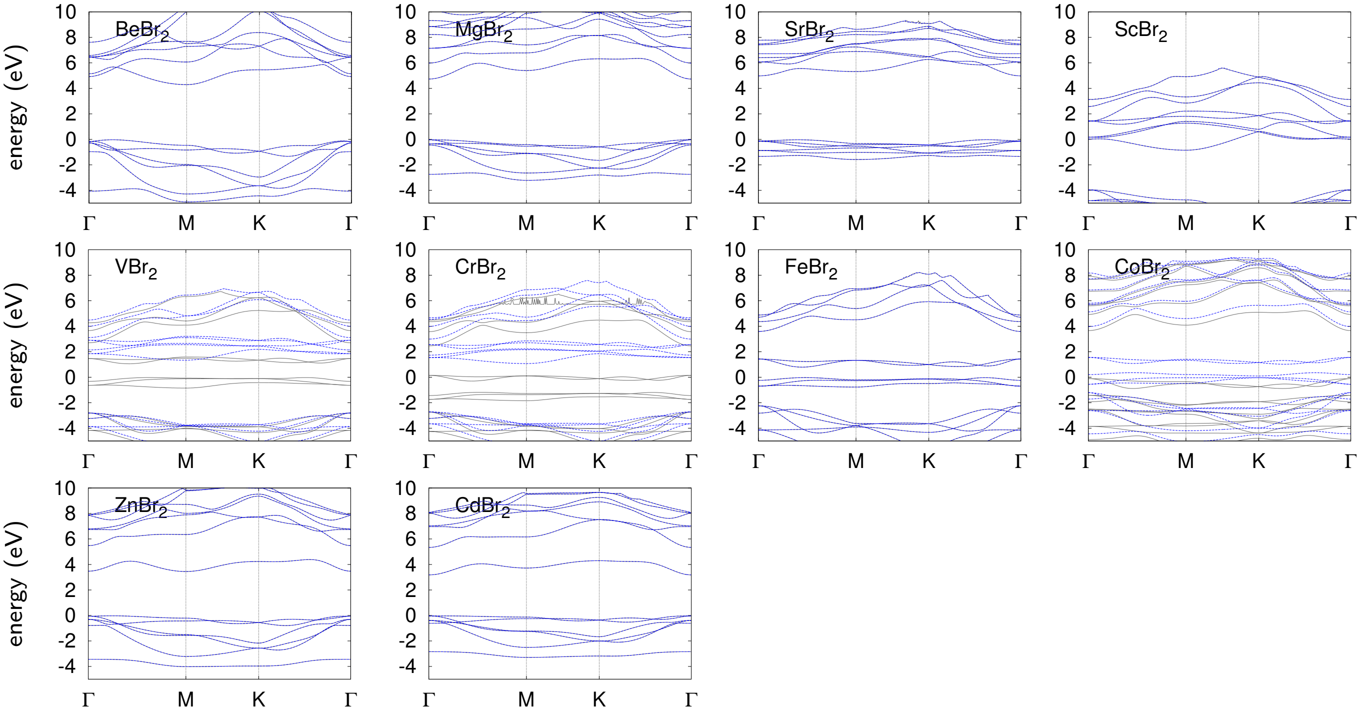

FIG. 5. Calculated band structures (PBE) for bromides discussed in main text. The grey solid and blue dotted lines correspond to the two spin states.

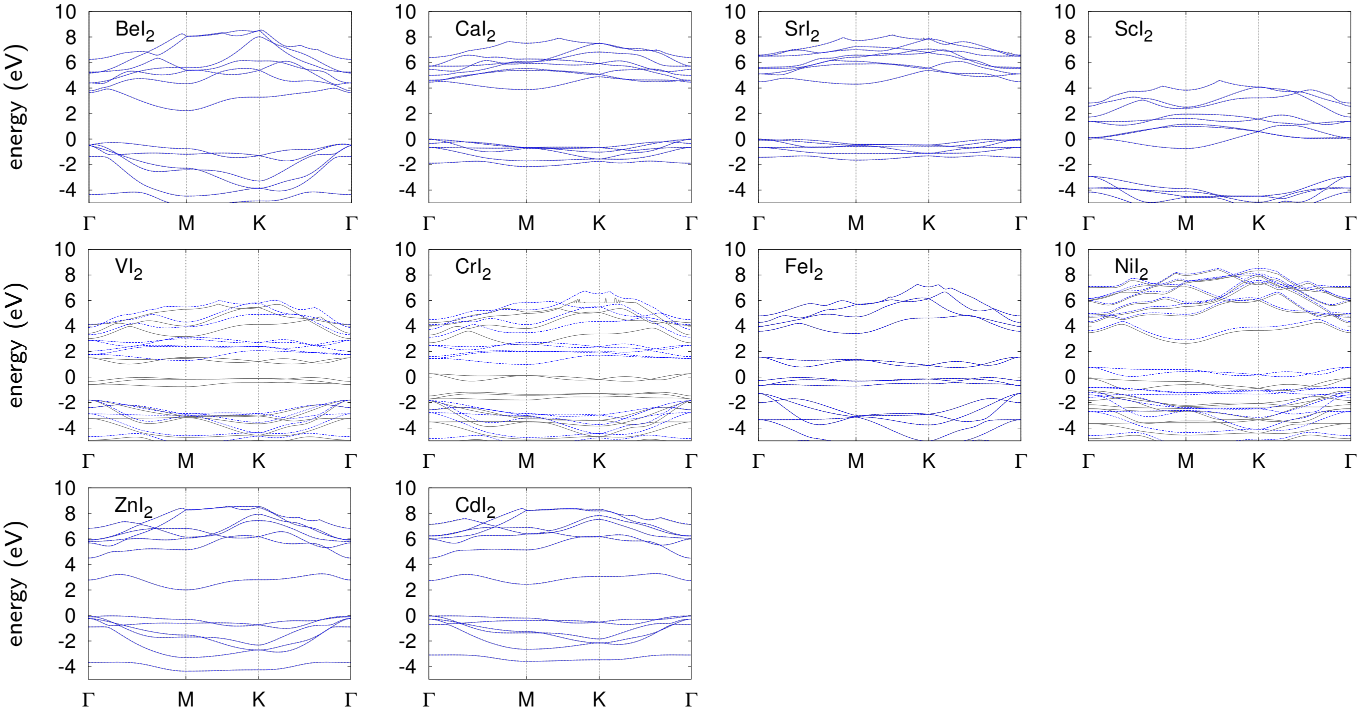

FIG. 6. Calculated band structures (PBE) for iodides discussed in main text. The grey solid and blue dotted lines correspond to the two spin states.