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The role of the A monovalent cation in the AVF_3 perovskite series. A quantum mechanical investigation.

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In this section, complementary material for the discussion in the main text is provided:

1. Table I provides the contribution of the polarization functions on the 5 A cations. For Li, Na, and K, then, the effect of adding a d shell is shown. For Rb and Cs, the energy lowering is due to the addition of a f shell. For Li, Na and K the d shell is added both in the cubic (Cs and Rb), and in the tetragonal (K) or orthorhombic (Li, Na) equilibrium geometries. Data refer to B3LYP, FM solution. In all cases the added shell contains a single Gaussian. The exponent of the polarization function has been optimized in the bulk.

2. Tables II, III, IV, V VI show the optimized Li, Na, K, Rb and Cs basis sets; the optimization is performed in the bulk, with B3LYP, for the FM solution. The V and F basis set has been optimized in KVF_3 bulk, and used as such for the other four systems.

3. Table VII reports the core and valence (and the lowest conduction) eigenvalues for the three kinds of atoms of the five systems, evaluated with B3LYP for the FM solution, at the equilibrium geometry of the most stable structure: cubic (Rb, Cs), or tetragonal (K), or orthorhombic (Na, Li). The width of the bands (δ) and the energy difference between the α and β eigenvalues (Δ) is also shown. Obviously, most of the *bands* are actually levels with width smaller than 0.1 eV.

All tables are referred to and commented in the main text.

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TABLE I. Effect of adding d (A=Li, Na, K) and f (Rb and Cs) polarization orbitals. ΔE is the total energy difference obtained with and without the polarization functions at fixed optimized geometry. The data to the left refer to the cubic structure; to the right, to the most stable space group (see text). The exponents of the optimized polarization shell is shown in the following tables. Q is the Mulliken population of the polarization shell. Energies are in E_h, ΔE in μE_h. Population in |e|.

	$Pm\bar{3}$ (221)				Pnma (62)		
	E	Q	ΔE		E	Q	ΔE
Li	-1251.276144	0.007	-1.3		-1251.324773	0.021	-1.0
Na	-1406.053857	0.013	-2.1		-1406.072297	0.017	-1.3
K	-1843.669071	0.038	-5.9		-1843.669146	0.039	-5.8
Rb	-4183.658627	0.004	-0.9				
Cs	-8800.175405	0.007	-1.9				

TABLE II. The K, V and F basis sets optimized (numerically) in KVF_3.
The optimization process stops when a full cycle of optimization lowers the total energy of the bulk by less than 1 μE_h; optimization performed for space group Pbmn (four formula units).

```
19  6
      0  0       8           2.0      1.0000
                170602.10967  0.00022
                 23423.76869  0.00201
                  4918.08613  0.01147
                  1305.24945  0.04985
                   404.40909  0.16260
                   142.61932  0.35178
                    55.32332  0.40572
                    22.35979  0.14772
      0  1       6           8.0      1.0000
                   471.67766  -0.00467 0.00626
                   113.04226  -0.05669 0.04548
                    36.60891  -0.14039 0.17447
                    13.65432   0.21493 0.37601
                     5.42563   0.71855 0.41160
                     2.02585   0.32366 0.16604
      0  1       5           8.0      1.0000
                    18.87356  -0.00342 -0.02775
                     6.48435  -0.27631 -0.06849
                     2.78914  -0.60990  0.24189
                     1.15389   1.07001  1.38192
                     0.42253   1.18745  1.27860
      0  1       1           0.0      1.0000
                     0.51160   1.00000  1.00000
      0  1       1           0.0      1.0000
                     0.15452   1.00000  1.00000
      0  3       1           0.0      1.0000
                     0.30473   1.00000
23  7
      0  0       8           2.0      1.0000
                243610.31337  0.00023
                 33706.54271  0.00204
                  7132.80340  0.01157
                  1906.39231  0.04990
                   592.63885  0.16306
                   209.18489  0.35407
                    81.52253  0.40504
                    33.04397  0.14371
      0  1       6           8.0      1.0000
                   714.98240  -0.00449 0.00660
                   171.50341  -0.05530 0.04806
                    56.07125  -0.14050 0.18607
                    21.21413   0.19583 0.40012
                     8.74267   0.70802 0.41590
                     3.60772   0.29757 0.13522
      0  1       4           8.0      1.0000
                    34.02706   0.01132 -0.02251
                    11.21250  -0.30640 -0.08367
                     4.81204  -0.76077  0.23245
                     2.04920   1.13284  1.22344
      0  1       1           0.0      1.0000
                     0.85592   1.00000  1.00000
      0  1       1           0.0      1.0000
                     0.32795   1.00000  1.00000
      0  3       4           3.0      1.0000
                    23.97650   0.03669
                     6.47729   0.18401
                     2.12869   0.42845
                     0.72089   0.51429
      0  3       1           0.0      1.0000
                     0.23477   1.00000
9   4
      0  0       7           2.0      1.0000
                 10139.60067  0.00110
                  1517.42324  0.00850
                   348.08291  0.04183
                   100.56220  0.14604
                    33.74770  0.33609
                    12.83710  0.40569
                     5.27944  0.16871
      0  1       3           8.0      1.0000
                    39.45194  -0.06901 0.07752
                     9.17932  -0.39853 0.45487
                     2.75061   0.48002 1.30646
      0  1       1           0.0      1.0000
                     0.86820   1.00000  1.00000
      0  1       1           0.0      1.0000
                     0.24838   1.00000  1.00000
```

TABLE III. The Li basis set optimized in $LiVF_3$

3	4			
	0	0	5	2.0 1.0000
			1207.38010	0.00155
			201.18462	0.00992
			45.76816	0.05585
			11.54912	0.24230
			3.11940	0.66414
	0	1	1	0.0 1.0000
			0.87435	1.00000 1.00000
	0	1	1	0.0 1.0000
			0.14960	1.00000 1.00000
	0	3	1	0.0 1.0000
			0.40845	1.00000

TABLE IV. The Na basis set optimized in $NaVF_3$

11	5			
	0	0	8	2.0 1.0000
			55701.72042	0.00023
			7945.78669	0.00194
			1683.28885	0.01119
			439.65696	0.05018
			133.30567	0.16677
			45.99796	0.36134
			17.66780	0.40167
			7.22365	0.14933
	0	1	5	8.0 1.0000
			108.46506	-0.00738 0.00871
			26.10566	-0.07257 0.05648
			8.40948	-0.08722 0.18921
			3.10995	0.31845 0.35247
			1.20577	0.61033 0.38252
	0	1	1	0.0 1.0000
			0.46702	1.00000 1.00000
	0	1	1	0.0 1.0000
			0.11512	1.00000 1.00000
	0	3	1	0.0 1.0000
			0.35851	1.00000

TABLE V. The Rb basis set optimized in $RbVF_3$

37	10			
	0 0	8	2.0	1.0000
		2850858.11809	0.00003	
		415753.92550	0.00030	
		71313.36763	0.00255	
		15645.53008	0.01409	
		4206.42720	0.06098	
		1279.89992	0.20518	
		422.60980	0.44897	
		146.09441	0.38337	
	0 1	6	8.0	1.0000
		4625.18760	-0.00033	0.00169
		1083.11959	-0.01075	0.01465
		341.74990	-0.07128	0.07645
		125.29215	-0.12744	0.25406
		49.98883	0.35681	0.48209
		20.61764	0.77457	0.38454
	0 1	5	8.0	1.0000
		75.50906	0.00116	-0.01604
		21.23088	-0.05942	-0.07551
		16.67282	-0.04588	0.14150
		8.08641	352.52995	0.62583
		5.32950	106.92995	0.61211
	0 1	3	8.0	1.0000
		7.11540	0.74932	-0.45559
		2.66216	0.19118	0.19639
		1.46383	0.02213	0.06671
	0 1	1	0.0	1.0000
		0.72691	1.00000	1.00000
	0 1	1	0.0	1.0000
		0.25325	1.00000	1.00000
	0 3	5	10.0	1.0000
		250.04613	0.00610	
		72.91736	0.04837	
		26.51837	0.19051	
		10.46395	0.41558	
		4.13361	0.47976	
	0 3	1	0.0	1.0000
		1.57935	0.99925	
	0 3	1	0.0	1.0000
		0.49255	0.99925	
	0 4	1	0.0	1.0000
		0.46697	1.00000	

TABLE VI. The Cs basi set optimized in $CsVF_3$

55	11			
	0 0	9	2.0	1.0000
		5371058.30078	0.00005	
		780235.96199	0.00040	
		166217.96247	0.00238	
		43056.24088	0.01130	
		12690.32695	0.04565	
		4128.37094	0.15065	
		1472.59933	0.35821	
		570.80952	0.48513	
		232.15700	0.23063	
	0 1	7	8.0	1.0000
		14813.73771	-0.00037	0.00115
		3459.82498	-0.00650	0.01026
		1091.07743	-0.05024	0.05724
		401.23611	-0.14503	0.21166
		165.00542	0.06736	0.47093
		74.12614	0.66416	0.52596
		34.75478	0.50279	0.22665
	0 1	6	8.0	1.0000
		362.87245	0.00616	-0.01286
		139.34470	-0.02466	-0.06984
		56.94712	-0.30068	-0.00730
		26.91024	-0.09427	0.77239
		12.80035	0.86557	1.36381
		6.28899	0.59226	0.53691
	0 3	6	10.0	1.0000
		444.19163	0.01298	
		133.01663	0.09115	
		50.23551	0.29264	
		21.15547	0.45088	
		9.49038	0.30392	
		4.13882	0.05614	
	0 1	3	8.0	1.0000
		10.22516	0.55576	-0.12044
		6.16664	0.24266	0.25117
		3.54524	0.04065	0.29157
	0 3	3	10.0	1.0000
		8.30737	0.19298	
		3.35715	0.54189	
		1.34214	0.42631	
	0 3	1	0.0	1.0000
		0.45394	1.00000	
	0 1	3	8.0	1.0000
		7.35954	0.10108	0.02690
		2.59709	0.88418	0.37490
		1.26647	0.61672	0.24353
	0 1	1	0.0	1.0000
		0.47820	1.00000	1.00000
	0 1	1	0.0	1.0000
		0.17933	1.00000	1.00000
	0 4	1	0.0	1.0000
		0.45425	1.00000	

	Li			Na			K			Rb			Cs		
	E_a	δ	Δ	E_a	δ	Δ	E_a	δ	Δ	E_a	δ	Δ	E_a	δ	Δ
Cs 1s													-34305.5	0.0	0.0
Rb 1s										-14790.2	0.0	0.0			
V 1s	-5350.8	0.0	0.0	-5350.9	0.0	0.0	-5350.9	0.0	0.0	-5351.1	0.0	0.0	-5350.9	0.0	0.0
K 1s							-3525.9	0.0	0.0						
Cs 2s													-5254.6	0.0	0.0
Cs 2p													-4949.6	0.0	0.0
Na 1s				-1040.8	0.0	0.0									
Rb 2s										-1956.8	0.0	0.0			
Rb 2p										-1775.7	0.0	0.0			
Cs 3s													-1093.9	0.0	0.0
Cs 3p													-963.7	0.0	0.0
Cs 3d													-721.9	0.0	0.0
F 1s	-666.0	0.3	0.0	-665.8	0.0	0.0	-665.7	0.0	0.0	-665.6	0.0	0.0	-665.0	0.0	0.0
V 2s	-599.0	0.0	1.0	-599.0	0.0	1.0	-599.0	0.0	1.0	-599.0	0.0	1.0	-599.0	0.0	1.0
V 2p	-503.7	0.0	0.8	-503.8	0.0	0.8	-503.8	0.0	0.8	-503.8	0.0	0.8	-503.8	0.0	0.8
Rb 3s										-289.1	0.0	0.0			
K 2s							-353.8	0.0	0.0						
K 2p							-281.4	0.0	0.0						
Rb 3p										-223.9	0.0	0.0			
Cs 4s													-203.1	0.0	0.0
Cs 4p													-155.8	0.0	0.0
Rb 3d										-105.2	0.0	0.0			
Cs 4d													-73.5	0.0	0.0
Na 2s				-54.9	0.0	0.0									
Li 1s	-48.5	0.0	0.0												
V 3s	-66.5	0.0	3.2	-66.5	0.0	3.2	-66.5	0.0	3.2	-66.5	0.0	3.2	-66.5	0.0	3.2
V 3p	-40.3	0.1	3.2	-40.3	0.1	3.3	-40.3	0.0	3.3	-40.3	0.0	3.4	-40.2	0.0	3.4
K 3s							-32.2	0.0	0.0						
Rb 4s										-27.3	0.2	0.0			
F 2s	-26.6	0.6	0.1	-26.6	0.5	0.0	-26.3	0.4	0.1	-26.1	0.4	0.1	-25.6	0.4	0.1
Na 2p				-26.6	0.5	0.0									
Cs 5s													-19.9	0.2	0.0
K 3p							-15.1	0.2	0.0						
Rb 4p										-12.0	0.6	0.0			
Cs 5p													-9.3	1.5	0.1
F 2p	-8.4	2.7	0.1	-8.3	2.5	0.1	-8.6	2.9	0.1	-8.5	2.9	0.1	-9.3	4.5	0.1
V t2g	-0.7	0.7	5.9	-0.8	0.8	5.1	-1.0	1.0	8.7	-1.0	1.0	7.6	-0.8	0.8	7.4
V eg	4.5	0.5	8.8	4.1	1.0	4.1	4.3	0.9	11.7	4.2	0.9	6.2	4.2	0.9	5.8
Na 3s				4.1	3.5	-2.0									
Li 2s	6.1	1.8	-1.0												
F 3s	6.1	1.8	0.3	5.6	2.0	5.7	6.0	2.6	0.9	9.3	1.5	0.7	8.9	1.5	0.6
Rb 5s										12.1	1.5	-0.7			
Cs 5s													8.9	1.5	0.6

TABLE VII. B3LYP FM core and valence eigenvalues (and lowest conduction ones) for the [Li-Cs]VF_3 system in the most stable structure. δ is the width of the band. Δ (in μE_h) is the maximum difference between the β and α eigenvalues. The horizontal line separates the occupied from the virtual levels.