Supplementary Information for

Structural evolution of Prussian Blue Analogue compounds $A_xMFe(CN)_6$ upon intercalation of Na and K

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Table S1. Gamma-point phonon modes calculated in the harmonic approximation for $FeFe(CN)_6$ at the optimised geometry.

MODES	EIGV	FREQUENCIES		MODES	EIGV	FREQUENCIES	
	(HARTREE**2)	(CM**-1)	(THZ)		(HARTREE**2)	(CM**-1)	(THZ)
1	-1.07E-20	0	0	85	3.45E-06	407.6423	12.2208
2	-5.62E-21	0	0	86	3.46E-06	408.1057	12.2347
3	-5.04E-21	0	0	87	3.46E-06	408.4221	12.2442
4	4.67E-08	47.4096	1.4213	88	3.46E-06	408.4568	12.2452
5	4.91E-08	48.618	1.4575	89	3.49E-06	409.7107	12.2828
6	4.97E-08	48.9077	1.4662	90	3.53E-06	412.4954	12.3663
7	5.31E-08	50.5724	1.5161	91	3.54E-06	412.8561	12.3771
8	5.39E-08	50.9619	1.5278	92	3.54E-06	412.8691	12.3775
9	5.51E-08	51.5322	1.5449	93	4.00E-06	439.0435	13.1622
10	8.09E-08	62.4156	1.8712	94	4.02E-06	440.0841	13.1934
11	9.02E-08	65.8992	1.9756	95	4.06E-06	441.9799	13.2502
12	9.17E-08	66.4511	1.9922	96	4.06E-06	442.0048	13.251
13	9.22E-08	66.6458	1.998	97	4.35E-06	457.7419	13.7228
14	9.45E-08	67.4619	2.0225	98	4.35E-06	457.936	13.7286
15	9.69E-08	68.33	2.0485	99	4.39E-06	459.7664	13.7835
16	1.59E-07	87.5173	2.6237	100	4.40E-06	460.1053	13.7936
17	1.60E-07	87.6935	2.629	101	4.40E-06	460.2779	13.7988
18	1.61E-07	88.1759	2.6434	102	4.40E-06	460.4367	13.8035
19	3.72E-07	133.8932	4.014	103	4.41E-06	460.8134	13.8148
20	3.74E-07	134.1583	4.022	104	4.44E-06	462.2321	13.8574
21	3.74E-07	134.2063	4.0234	105	4.44E-06	462.361	13.8612
22	3.82E-07	135.6785	4.0675	106	4.45E-06	462.8029	13.8745
23	3.85E-07	136.1762	4.0825	107	4.46E-06	463.5201	13.896
24	3.85E-07	136.2589	4.0849	108	4.47E-06	463.8463	13.9058
25	5.25E-07	158.9939	4.7665	109	4.49E-06	464.975	13.9396
26	5.55E-07	163.4927	4.9014	110	4.50E-06	465.5613	13.9572
27	5.55E-07	163.5464	4.903	111	4.55E-06	468.3133	14.0397
28	5.61E-07	164.4333	4.9296	112	4.57E-06	469.0014	14.0603
29	5.63E-07	164.7025	4.9377	113	4.60E-06	470.7754	14.1135
30	5.65E-07	165.0115	4.9469	114	4.62E-06	471.6086	14.1385
31	5.90E-07	168.5671	5.0535	115	4.63E-06	472.3349	14.1602
32	5.90E-07	168.603	5.0546	116	4.65E-06	473.1864	14.1858
33	6.19E-07	172.6637	5.1763	117	4.66E-06	473.6575	14.1999
34	6.25E-07	173.5378	5.2025	118	4.67E-06	474.3312	14.2201
35	6.25E-07	173.5669	5.2034	119	4.68E-06	474.57	14.2273
36	6.32E-07	174.5343	5.2324	120	4.72E-06	476.8493	14.2956
37	6.33E-07	174.6438	5.2357	121	4.95E-06	488.1237	14.6336
38	6.37E-07	175.1427	5.2506	122	4.97E-06	489.0153	14.6603
39	6.54E-07	177.4705	5.3204	123	4.98E-06	489.5293	14.6757
40	6.92E-07	182.6304	5.4751	124	4.98E-06	489.5489	14.6763
41	6.93E-07	182.6738	5.4764	125	4.99E-06	490.4121	14.7022
42	6.93E-07	182.6951	5.4771	126	5.00E-06	490.4971	14.7047
43	7.03E-07	183.9775	5.5155	127	5.00E-06	490.6757	14.7101
44	7.03E-07	183.9987	5.5161	128	5.00E-06	490.8568	14.7155
45	7.03E-07	184.0202	5.5168	129	5.92E-06	533.7631	16.0018
46	9.06E-07	208.918	6.2632	130	5.92E-06	533.8784	16.0053
47	9.41E-07	212.9412	6.3838	131	5.93E-06	534.5109	16.0242
48	9.42E-07	213.0342	6.3866	132	5.94E-06	534.7074	16.0301
49	9.61E-07	215.1826	6.451	133	5.94E-06	534.8657	16.0349
50	9.62E-07	215.305	6.4547	134	5.98E-06	536.5169	16.0844
51	9.87E-07	218.0018	6.5355	135	5.98E-06	536.6948	16.0897
52	1.19E-06	239.5714	7.1822	136	5.99E-06	537.0481	16.1003
53	1.24E-06	244.4695	7.329	137	7.00E-06	580.6869	17.4086
54	1.26E-06	245.9676	7.3739	138	7.00E-06	580.7966	17.4118
55	1.31E-06	250.8097	7.5191	139	7.01E-06	581.2311	17.4249
56	1.31E-06	251.0941	7.5276	140	7.01E-06	581.2703	17.426
57	1.32E-06	251.7849	7.5483	141	7.02E-06	581.3504	17.4284

58	1.32E-06	251.9796	7.5542	142	7.02E-06	581.6145	17.4364
59	1.32E-06	252.0365	7.5559	143	7.05E-06	582.6415	17.4672
60	1.33E-06	252.9407	7.583	144	7.07E-06	583.5355	17.494
61	1.39E-06	258.3548	7.7453	145	1.07E-04	2274.82	68.1974
62	1.41E-06	260.4973	7.8095	146	1.07E-04	2274.914	68.2002
63	1.47E-06	265.9137	7.9719	147	1.08E-04	2275.066	68.2048
64	1.57E-06	275.2894	8.253	148	1.08E-04	2276.253	68.2404
65	1.57E-06	275.3801	8.2557	149	1.08E-04	2276.534	68.2488
66	1.61E-06	278.0197	8.3348	150	1.08E-04	2280.682	68.3731
67	1.61E-06	278.4152	8.3467	151	1.08E-04	2281.009	68.3829
68	1.62E-06	279.2259	8.371	152	1.08E-04	2281.089	68.3853
69	1.62E-06	279.2644	8.3721	153	1.08E-04	2281.285	68.3912
70	1.89E-06	301.9647	9.0527	154	1.08E-04	2281.832	68.4076
71	1.89E-06	302.063	9.0556	155	1.08E-04	2281.885	68.4092
72	1.90E-06	302.3213	9.0634	156	1.08E-04	2282.027	68.4134
73	2.31E-06	333.4105	9.9954	157	1.08E-04	2282.197	68.4185
74	2.34E-06	335.8031	10.0671	158	1.08E-04	2282.295	68.4215
75	2.34E-06	335.8699	10.0691	159	1.08E-04	2282.307	68.4218
76	2.35E-06	336.2011	10.0791	160	1.08E-04	2282.644	68.4319
77	2.37E-06	337.5001	10.118	161	1.08E-04	2282.824	68.4373
78	2.37E-06	337.8883	10.1296	162	1.10E-04	2304.17	69.0773
79	2.85E-06	370.4919	11.1071	163	1.10E-04	2304.197	69.0781
80	2.85E-06	370.6955	11.1132	164	1.10E-04	2304.275	69.0804
81	2.85E-06	370.7507	11.1148	165	1.11E-04	2313.326	69.3518
82	2.90E-06	373.7281	11.2041	166	1.11E-04	2313.407	69.3542
83	2.91E-06	374.1707	11.2174	167	1.11E-04	2313.787	69.3656
84	2.91E-06	374.1841	11.2178	168	1.11E-04	2316.681	69.4524

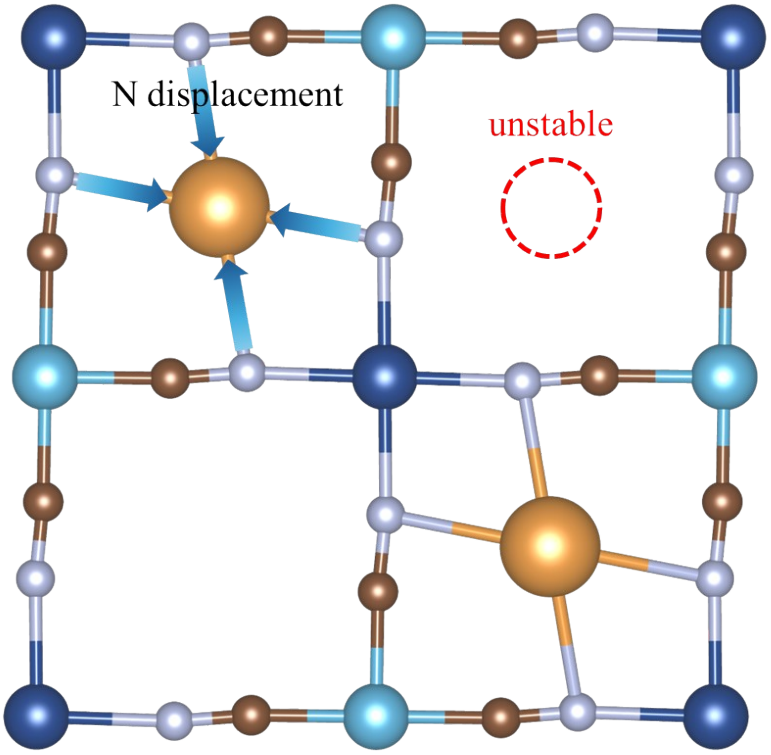

Figure S1. Schematic of stable and unstable position for intercalant A induced by N-displacement during 2-D distortion.

Example input file.

All calculations have been performed with the code CRYSTAL17 available from www.crystal.unito.it. An example input file, including basis set and computational parameters, is included below:

```
Prussian Blue, octah
CRYSTAL
0 0 0
1
10.052904 10.004958 10.051974 89.271492 87.178955 90.676559
56
125     0.000001        0.500000        0.000000
125     0.500001        0.500000        0.500000
125     0.000001        0.000001        0.500001
125     0.500000        0.000001        0.000001
126     0.000001        0.000001        0.000001
126     0.500001        0.000001        0.500001
126     0.500000        0.500000        0.000000
126     0.000000        0.500000        0.500000
6       0.040355        0.183069        0.972897
6       0.540488        0.183058        0.472961
6       0.973068        0.316924        0.540494
6       0.472780        0.316940        0.040474
6       0.959645        0.816931        0.027103
6       0.459512        0.816942        0.527039
6       0.026932        0.683076        0.459506
6       0.527220        0.683060        0.959526
6       0.819666        0.035228        0.969295
6       0.319681        0.035308        0.469305
6       0.969084        0.464779        0.319721
6       0.469256        0.464818        0.819692
6       0.180334        0.964772        0.030705
6       0.680319        0.964692        0.530695
6       0.030916        0.535221        0.680279
6       0.530744        0.535182        0.180308
7       0.062145        0.297514        0.960036
7       0.562352        0.297494        0.460124
7       0.960244        0.202472        0.562309
7       0.459908        0.202486        0.062264
7       0.937855        0.702486        0.039964
7       0.437648        0.702506        0.539876
7       0.039756        0.797528        0.437691
7       0.540092        0.797514        0.937736
6       0.967459        0.030779        0.183871
6       0.467554        0.030746        0.683876
6       0.683845        0.469007        0.967509
6       0.183873        0.469239        0.467379
6       0.032541        0.969221        0.816129
6       0.532446        0.969254        0.316124
6       0.316155        0.530993        0.032491
6       0.816127        0.530761        0.532621
7       0.707344        0.056606        0.954371
7       0.207346        0.056327        0.454075
7       0.954112        0.443375        0.207423
7       0.454381        0.443420        0.707377
7       0.292656        0.943394        0.045629
7       0.792654        0.943673        0.545925
7       0.045888        0.556625        0.792577
```

```
7          0.545619        0.556580        0.292623
7          0.950618        0.048967        0.297926
7          0.450800        0.048927        0.797940
7          0.798006        0.451530        0.950520
7          0.297967        0.451133        0.450761
7          0.049382        0.951033        0.702074
7          0.549200        0.951073        0.202060
7          0.201994        0.548470        0.049480
7          0.702034        0.548867        0.549239
OPTGEOM
MAXTRADIUS
0.5
ENDOPT
END
26 8
0 0 8 2.0 1.0
 315379.0 0.000227
 45690.0 0.0019
 9677.3 0.0111
 2520.88 0.0501
 759.746 0.1705
 262.964 0.36924
 102.801 0.4033
 42.9733 0.1434
0 1 6 8.0 1.0
 798.262 -0.0052 0.00850
 191.162 -0.068 0.0608
 63.6885 -0.1314 0.2114
 25.3625 0.2517 0.3944
 10.7338 0.6433 0.398
 3.764 0.2825 0.2251
0 1 4 8.0 1.0
 48.1434 0.0122 -0.0215
 17.4579 -0.2278 -0.085
 6.9972 -0.8801 0.201
 3.0791 0.9755 1.3024
0 1 1 0.0 1.0
 1.3137 1.0 1.0
0 1 1 0.0 1.0
 0.5625 1.0 1.0
0  1  1  0.0  1.0
 0.20   1.0 1.0
0 3 4 6.0 1.0
 30.4821 0.0583
 8.692 0.2591
 3.1008 0.5162
 1.1709 0.5656
0 3 1 0.0 1.0
 0.4345 1.0
126 8
0 0 8 2.0 1.0
 315379.0 0.000227
 45690.0 0.0019
 9677.3 0.0111
 2520.88 0.0501
 759.746 0.1705
 262.964 0.36924
 102.801 0.4033
 42.9733 0.1434
0 1 6 8.0 1.0
```

798.262 -0.0052 0.00850
191.162 -0.068 0.0608
63.6885 -0.1314 0.2114
25.3625 0.2517 0.3944
10.7338 0.6433 0.398
3.764 0.2825 0.2251
0 1 4 8.0 1.0
48.1434 0.0122 -0.0215
17.4579 -0.2278 -0.085
6.9972 -0.8801 0.201
3.0791 0.9755 1.3024
0 1 1 0.0 1.0
1.3137 1.0 1.0
0 1 1 0.0 1.0
0.5625 1.0 1.0
0 1 1 0.0 1.0
0.20 1.0 1.0
0 3 4 5.0 1.0
30.4821 0.0583
8.692 0.2591
3.1008 0.5162
1.1709 0.5656
0 3 1 0.0 1.0
0.4345 1.0
25 7
0 0 8 2.0 1.0
292601.0 0.000227
42265.0 0.0019
8947.29 0.0111
2330.32 0.0501
702.047 0.1705
242.907 0.3691
94.955 0.4035
39.5777 0.1437
0 1 6 8.0 1.0
732.14 -0.0053 0.0086
175.551 -0.0673 0.0612
58.5093 -0.1293 0.2135
23.129 0.2535 0.4018
9.7536 0.6345 0.4012
3.4545 0.2714 0.2222
0 1 4 8.0 1.0
38.389 0.0157 -0.0311
15.4367 -0.2535 -0.0969
6.1781 -0.8648 0.2563
2.8235 0.9337 1.6552
0 1 1 0 1.0
1.2086 1.0 1.0
0 1 1 0.0 1.0
0.4986 1.0 1.0
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6.1674 0.3044
2.0638 0.5469
0.7401 0.5102
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0.249 1.0
125 7
0 0 8 2.0 1.0
292601.0 0.000227

42265.0 0.0019
8947.29 0.0111
2330.32 0.0501
702.047 0.1705
242.907 0.3691
94.955 0.4035
39.5777 0.1437
0 1 6 8.0 1.0
732.14 -0.0053 0.0086
175.551 -0.0673 0.0612
58.5093 -0.1293 0.2135
23.129 0.2535 0.4018
9.7536 0.6345 0.4012
3.4545 0.2714 0.2222
0 1 4 8.0 1.0
38.389 0.0157 -0.0311
15.4367 -0.2535 -0.0969
6.1781 -0.8648 0.2563
2.8235 0.9337 1.6552
0 1 1 0 1.0
1.2086 1.0 1.0
0 1 1 0.0 1.0
0.4986 1.0 1.0
0 3 4 4.0 1.0
22.5929 0.0708
6.1674 0.3044
2.0638 0.5469
0.7401 0.5102
0 3 1 0.0 1.0
0.249 1.0
11 5
0 0 8 2. 1.
56700. 0.000225
8060. 0.00191
1704. 0.0105
443.6 0.05006
133.1 0.1691
45.8 0.3658
17.75 0.3998
7.38 0.1494
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25.33 -0.0798 0.0639
7.80 -0.0793 0.2074
3.00 0.3056 0.3398
1.289 0.5639 0.3726
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0.543731341992 1. 1.
0 1 1 0. 1.
0.215680639594 1. 1.
0 3 1 0. 1.
0.778535164031 1.
19 6
0 0 8 2. 1.
172500. 0.000220
24320. 0.00192
5140. 0.01109
1343.9 0.04992
404.5 0.1702
139.4 0.3679

```
 54.39 0.4036
 22.71 0.1459
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 402.0 -0.00603 0.00841
 93.5 -0.0805 0.0602
 30.75 -0.1094 0.2117
 11.91 0.258 0.3726
 5.167 0.684 0.4022
 1.582 0.399 0.186
0 1 5 8. 1.
 17.35 -0.0074 -0.0321
 7.55 -0.129 -0.062
 2.939 -0.6834 0.1691
 1.19 1.08 1.500
 0.674 1.03 1.060
0 1 1 0. 1.
 0.389 1. 1.
0 1 1 0. 1.
 0.216 1. 1.
0 3 3 0. 1.
 3.94 0.160
 1.072 0.313
 0.394 0.406
6 5
0 0 6 2. 1.
    4563.2400000          0.00196665
     682.0240000          0.0152306
     154.9730000          0.0761269
      44.4553000          0.2608010
      13.0290000          0.6164620
       1.8277300          0.2210060
0 1 3 5. 1.
      20.9642000          0.1146600          0.0402487
       4.8033100          0.9199990          0.2375940
       1.4593300         -0.00303068         0.8158540
0 1 1 0. 1.
       0.4834560          1.0000000          1.0000000
0 1 1 0. 1.
       0.1455850          1.0000000          1.0000000
0 3 1 0. 1.
       0.6260000          1.0000000
7 5
0 0 6 2. 1.
    6293.4800000          0.00196979
     949.0440000          0.0149613
     218.7760000          0.0735006
      63.6916000          0.2489370
      18.8282000          0.6024600
       2.7202300          0.2562020
0 1 3 5. 1.
      30.6331000          0.1119060          0.0383119
       7.0261400          0.9216660          0.2374030
       2.1120500         -0.00256919         0.8175920
0 1 1 0. 1.
       0.6840090          1.0000000          1.0000000
0 1 1 0. 1.
       0.2008780          1.0000000          1.0000000
0 3 1 0. 1.
       0.9130000          1.0000000
8 5
```

```
0 0 6 2. 1.
    8588.5000000           0.00189515
    1297.2300000           0.0143859
     299.2960000           0.0707320
      87.3771000           0.2400010
      25.6789000           0.5947970
       3.7400400           0.2808020
0 1 3 6. 1.
      42.1175000           0.1138890           0.0365114
       9.6283700           0.9208110           0.2371530
       2.8533200          -0.00327447          0.8197020
0 1 1 0. 1.
       0.9056610           1.0000000           1.0000000
0 1 1 0. 1.
       0.2556110           1.0000000           1.0000000
0 3 1 0. 1.
       1.2920000           1.0000000
1 4
0 0 3 1. 1.
      33.8650000           0.0254938
       5.0947900           0.1903730
       1.1587900           0.8521610
0 0 1 0. 1.
       0.3258400           1.0000000
0 0 1 0. 1.
       0.1027410           1.0000000
0 2 1 0. 1.
       0.7500000           1.0000000
99 0
END
DFT
SPIN
PBE0
END
ATOMSPIN
8
1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1
TOLINTEG
7 7 7 7 14
SHRINK
4 4
TOLDEE
7
SPINLOCK
20 -1
THREDIIS
0.001
MAXCYCLE
500
FMIXING
95
END
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