Electronic supplementary information

Insight into the Magnetic Moment of Iron Borides: Theoretical Consideration from Local Coordinative and Electronic Environment

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Table S1. The structure parameters and magnetic moment of iron borides calculated by different method. Among three method, the optimization results obtained by GGA-PBE get closer to the experiment and other DFT results.

Phases	Structure parameters	LDA	PBE	PW91	Exp.	Other DFT work[a]
o-Fe_3B	*a*	5.011	5.398	5.379	5.397[a]	5.393
	b	6.485	6.652	6.638	6.648[a]	6.656
	c	4.254	4.371	4.385	4.368[a]	4.380
	V/atom	8.640	9.809	9.786	9.80[a]	9.826
	μ_{Fe}	-0.46	2.08	2.04	1.95[b]	2.08
t-Fe_3B	*a*=*b*	8.202	8.547	8.537	8.674[c]	8.551
	c	4.076	4.244	4.236	4.313[c]	4.240
	V/atom	8.569	9.688	9.648	10.141[c]	9.688
	μ_{Fe}	0.24	2.05	1.99	1.99[b]	2.02
Fe_2B	*a*=*b*	4.941	5.054	5.050	5.120[d]	5.056
	c	4.039	4.230	4.230	4.259[d]	4.232
	V/atom	8.217	9.004	8.990	9.304[d]	9.015
	μ_{Fe}	1.12	1.91	1.86	1.95[e]	1.90
FeB	*a*	5.225	5.407	5.405	5.495[d]	5.413
	b	2.935	2.944	2.950	2.941[d]	2.948
	c	3.924	3.994	3.992	4.048[d]	3.998
	V/atom	7.522	7.947	7.956	8.177[d]	7.975
	μ_{Fe}	1.06	1.22	1.20	1.26[e]	1.25
FeB_2	*a*	4.744	4.813	4.817	4.819[a]	4.816
	b	4.738	4.805	4.798	4.807[a]	4.807
	c	3.675	3.738	3.744	3.742[a]	3.740
	V/atom	6.884	7.204	7.211	7.220[a]	7.215
	μ_{Fe}	0.00	0.00	0.00	0.00[f]	0.00
FeB_4	*a*	4.439	4.521	4.523	4.579[g]	4.521
	b	5.223	5.284	5.274	5.298[g]	5.284
	c	2.965	3.006	3.005	3.000[g]	3.006
	V/atom	6.874	7.181	7.168	7.275[g]	7.181
	μ_{Fe}	0.00	0.00	0.00	0.00[f]	0.00

[a]reference[1] [b]reference[2] [c]reference[3] [d]reference[4] [e]reference[5] [f]reference[6] [g]reference[7]

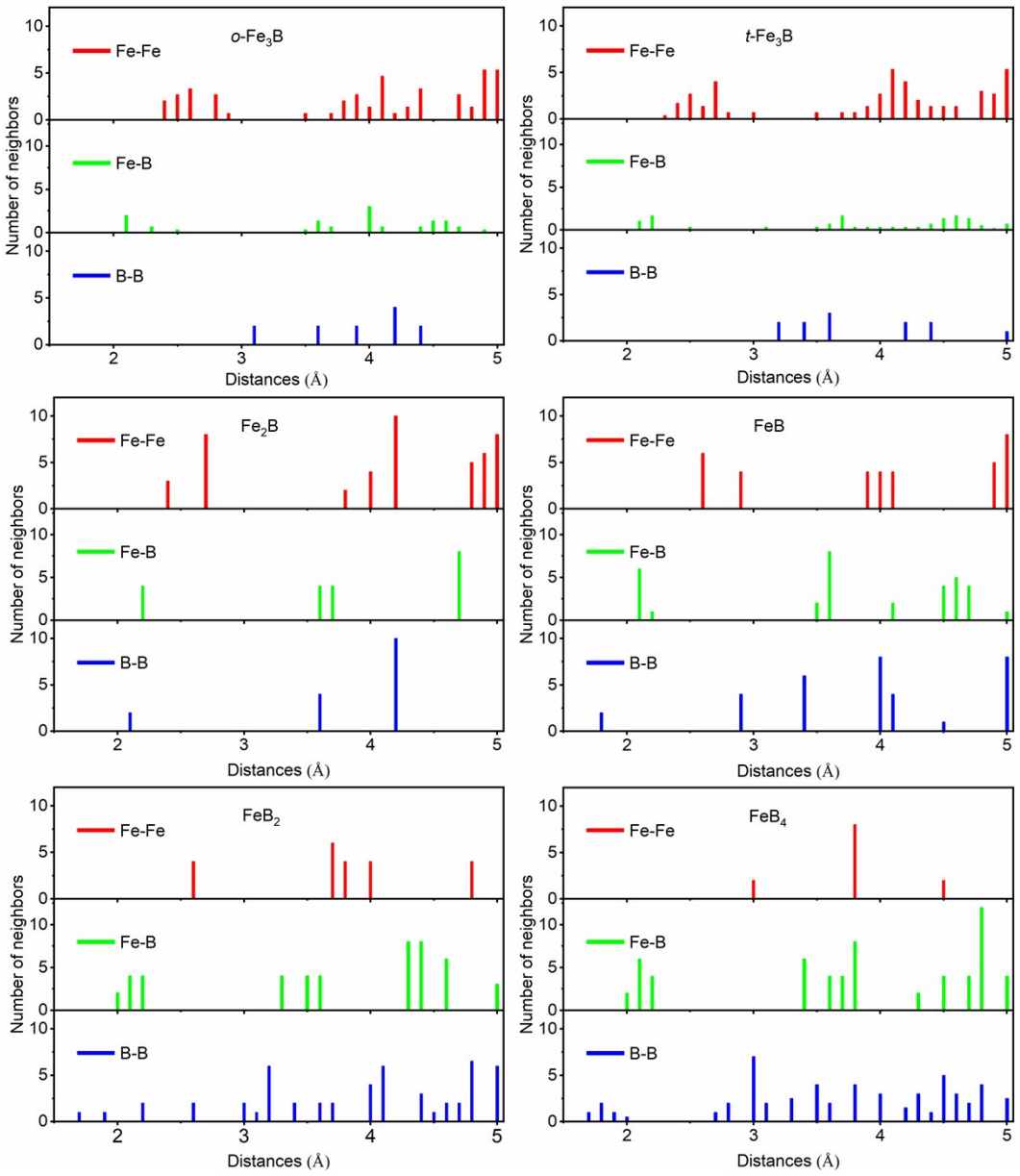

Fig. S1. The average number of neighbors at different distances in the unit cell.

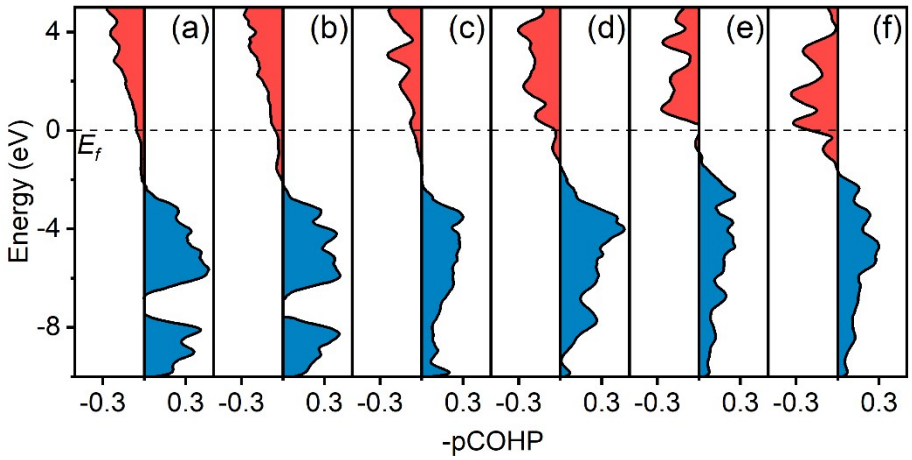

Fig. S2. The projected Crystal Orbital Hamilton Population analysis of Fe-B bonds in (a) *o*-Fe_3B (b) *t*- Fe_3B (c) Fe_2B (d) FeB (e) FeB_2 (f) FeB_4. Red and blue fill region represent the anti-bonding and bonding contribution, respectively. Dash line represent the Fermi level which is set to zero.

Table S2. The electronic and bonding parameters of iron borides. Δq and ICOHP represent the net charge and integral COHP of Fe atoms.

Iron boride	B/Fe ratio	Central Fe	Δq (e)	ICOHP
α-Fe	-	Fe1	0.00	-
o-Fe_3B	0.33	Fe1	-0.34	-1.26
		Fe2	-0.21	-0.53
t-Fe_3B	0.33	Fe1	-0.18	-0.34
		Fe2	-0.29	-0.52
		Fe3	-0.19	-0.52
Fe_2B	0.50	Fe1	-0.28	-0.97
FeB	1.00	Fe1	-0.42	-1.66
FeB_2	2.00	Fe1	-0.24	-1.07
FeB_4	4.00	Fe1	-0.43	-1.34

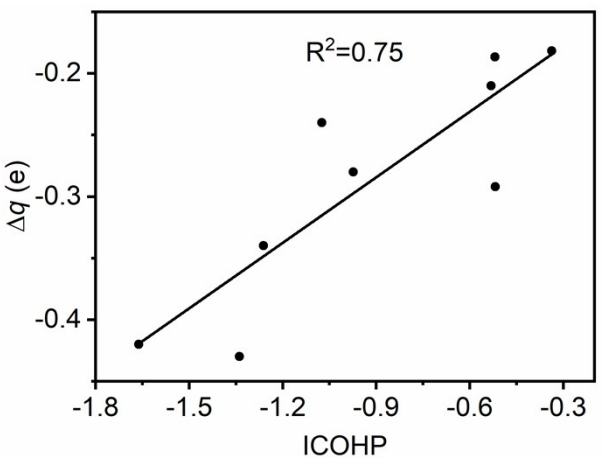

Fig. S3. Correlation between integrated COHP (ICOHP) and bader charge.

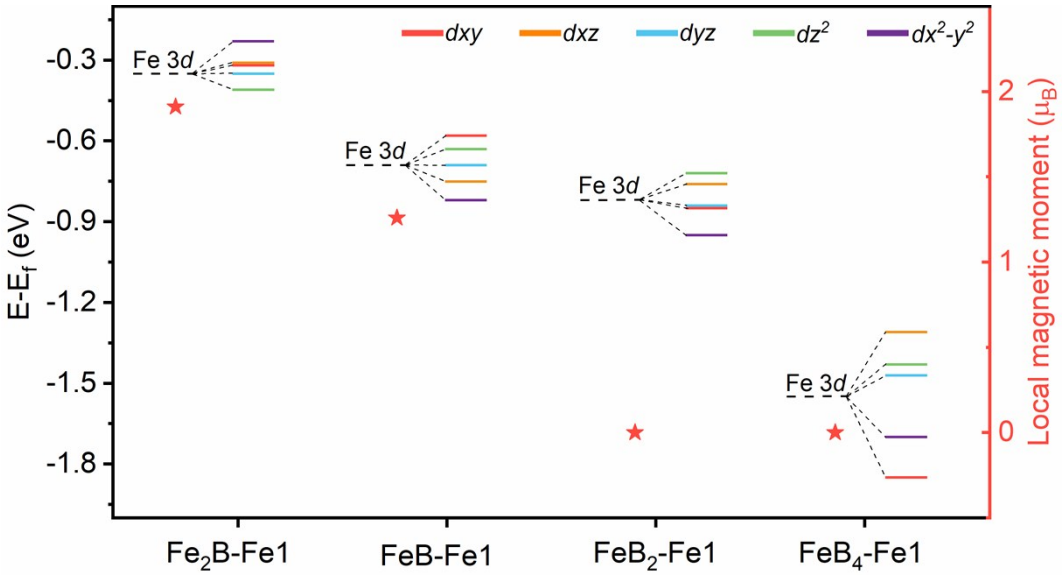

Fig.S4. The Fe 3*d* orbital energy level and local magnetic moments of different Fe atoms in iron borides. Red marks represent local magnetic moment of relevant Fe atoms.

Table S3 The band gap of FeB_2 that calculated with different functionals.

Functionals	PBE (This work)	PBE+U				HSE06	PBE (Phys. Rev. Lett. **2010**, 105, 217003)
		U = 2 eV	U = 3 eV	U = 4 eV	U = 5 eV		
Band gap (eV)	0.45	0.53	0.59	0.65	0.65	1.03	~0.5

References

1 L.-H. Li, W.-L. Wang, L. Hu and B.-B. Wei, *Intermetallics*, 2014, **46**, 211-221.

2 Y. Kong and F. Li, *Phys. Rev. B*, 1997, **56**, 3153-3158.

3 Y. Li and R. P. Chang, *J. Am. Chem. Soc.*, 2006, **128**, 12778-12784.

4 C. Kapfenberger, B. Albert, R. Pottgen and H. Huppertz, *Z. Kristallogr.*, 2006, **221**, 477-481.

5 W. Y. Ching, Y.-N. Xu, B. N. Harmon, J. Ye and T. C. Leung, *Phy. Rev. B*, 1990, **42**, 4460-4470.

6 A. N. Kolmogorov, S. Shah, E. R. Margine, A. F. Bialon, T. Hammerschmidt and R. Drautz, *Phys. Rev. Lett.*, 2010, **105**, 217003.

7 H. Gou, N. Dubrovinskaia, E. Bykova, A. A. Tsirlin, D. Kasinathan, W. Schnelle, A. Richter, M. Merlini, M. Hanfland, A. M. Abakumov, D. Batuk, G. Van Tendeloo, Y. Nakajima, A. N. Kolmogorov and L. Dubrovinsky, *Phys. Rev. Lett.*, 2013, **111**, 157002.