
Supplementary Material for

Interplanar magnetic orders and symmetry-tuned zero thermal expansion in kagomé metal (Zr,Ta)Fe₂

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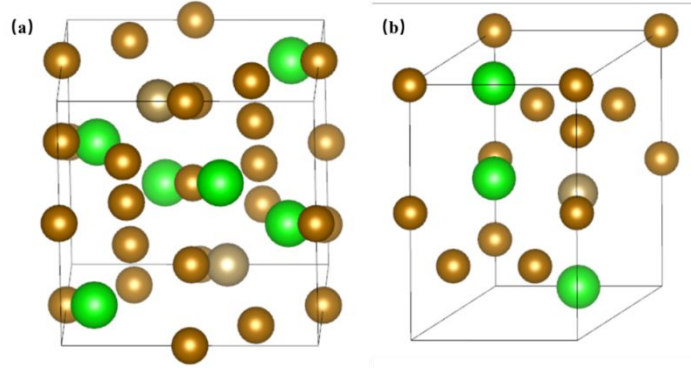


Figure S1. Two crystal structure models of $\text{Zr}_{0.75}\text{Ta}_{0.25}\text{Fe}_2$ with approximate free energy based on first principles calculation.

First-principles calculations were carried out via Vienna ab initio package (VASP)^[1] program by using projected augmented wave (PAW) potential^[2] with a cutoff energy of 400 eV. The Perdew-Burke-Ernzerhof (PBE) functional was used within the formulation of generalized gradient approximation (GGA)^[3,4] for the exchange-correlation term. As the unit cell of cubic phase $(\text{Zr,Ta})\text{Fe}_2$ contains 8 iron atoms, the model was built from the approximate composition unit cell of $\text{Zr}_{0.75}\text{Ta}_{0.25}\text{Fe}_2$ in order to set integral Zr (3) and Ta (1) atoms in the unit cell of $(\text{Zr,Ta})\text{Fe}_2$ (Figure S1). The reciprocal space was sampled by the gamma point in the Brillouin zone with a grid of $9 \times 9 \times 4$. The energy difference of 1.0×10^{-7} eV per atom and the max force of 0.02 eV/Å were set as the convergence criteria for geometry optimization and subsequent density of states. The magnetic moment of antiferromagnetic (AFM) and ferromagnetic (FM) orderings were set for different phases of $(\text{Zr,Ta})\text{Fe}_2$ in order to estimate the accurate electric structures.

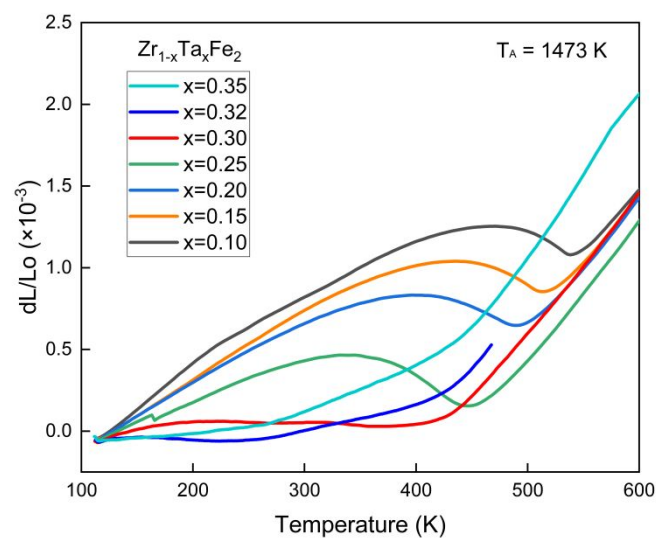


Figure S2. Apparent linear thermal expansion of $\text{Zr}_{1-x}\text{Ta}_x\text{Fe}_2$ measured by dilatometer with $T_A = 1473 \text{ K}$.

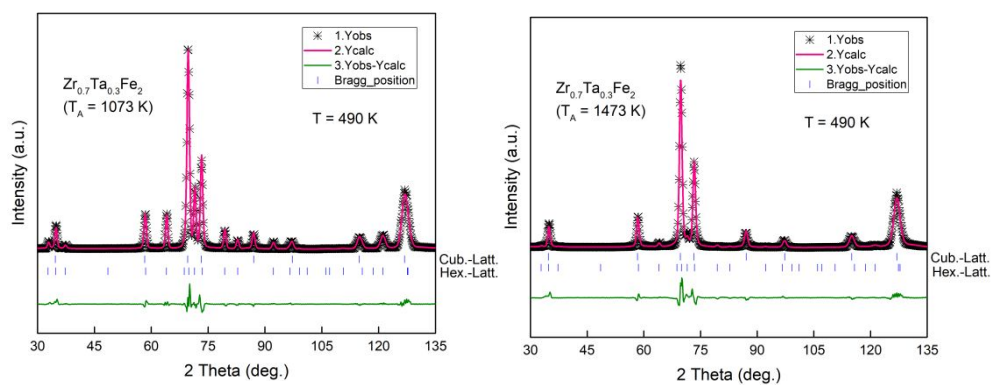


Figure S3. Rietveld refinements of high temperature NPD patterns of $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ with various annealing temperature at 1073 K, 1473 K, respectively.

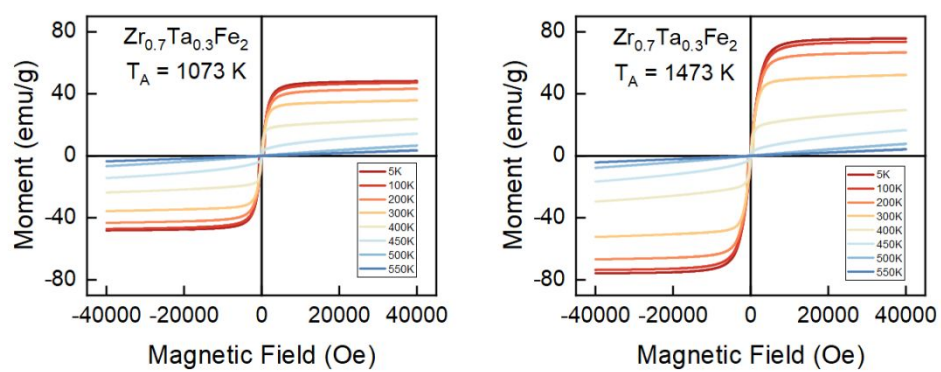


Figure. S4. Magnetization curves (M–H) of $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds at various temperatures.

Table S1. Room temperature fitted parameters of Mossbauer spectra of $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds with $T_A \sim 1073$ K.

	Site	Isomer Shift (mm/s)	Quadrupole Splitting (mm/s)	Magnetic Hyperfine Field (T)	Ratio (%)
$\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ $T_A \sim 1073$ K	Fe_{6h}	-0.22	0.17	6.4	35.7
	Fe_{2a}	-0.21	0.32	0	11.9
	Fe_{16d}	-0.19	0.03	15.1	39.3
	Fe_{16d}	-0.20	0.05	17.0	13.1

Table S2. Room temperature fitted parameters of Mossbauer spectra of $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds with $T_A \sim 1473$ K.

	Site	Isomer Shift (mm/s)	Quadrupole Splitting (mm/s)	Magnetic Hyperfine Field (T)	Ratio (%)
$\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ $T_A \sim 1473$ K	Fe_{6h}	-0.21	0.18	6.6	9.0
	Fe_{2a}	-0.21	0.32	0	3.1
	Fe_{16d}	-0.21	0.08	15.2	66.0
	Fe_{16d}	-0.19	0.06	17.0	21.9

Table S3. Hyperfine field calculations determined by the ^{57}Fe Mössbauer spectrum of $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ with $T_A \sim 1073$ K and ~ 1473 K, including the ratio and hyperfine field of each Fe atoms.

$T_A \sim 1073$ K			$T_A \sim 1473$ K		
Site	Ratio (%)	Hyperfine field (T)	Site	Ratio (%)	Hyperfine field (T)
Fe_{6h}	35.7	6.4	Fe_{6h}	9.0	6.6
Fe_{2a}	11.9	0	Fe_{2a}	3.1	0
Fe_{16d}	39.3	15.1	Fe_{16d}	66.0	15.2
Fe_{16d}	13.1	17.0	Fe_{16d}	21.9	17.0
Total	100.0	FM (H): 21.0	Total	100.0	FM (H): 28.7
$\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$		AFM (H): 16.4	$\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$		AFM (H): 27.5

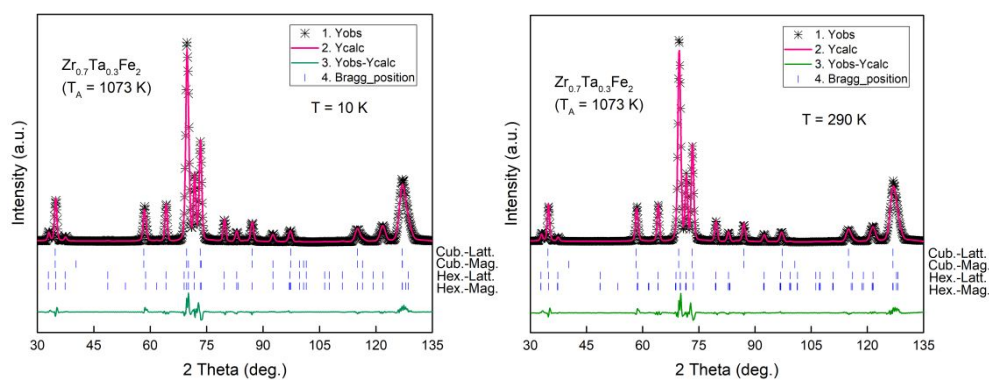


Figure S5. Rietveld refinements of low temperature NPD patterns for $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds with annealing temperature at 1073 K.

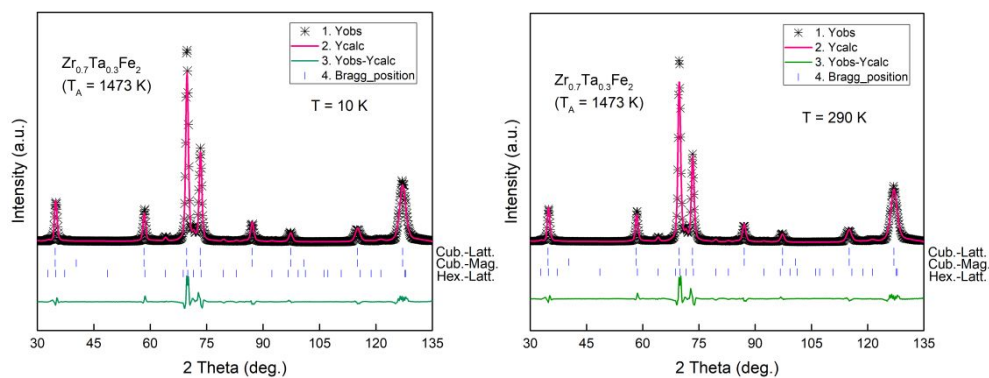


Figure S6. Rietveld refinements of low temperature NPD patterns for $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds with annealing temperature at 1473 K.

Table S4. Temperature dependence of magnetic moments (M_{Fe}) determined by NPD for $\text{Fe}_{16\text{d}}$, $\text{Fe}_{6\text{h}}$ and $\text{Fe}_{2\text{a}}$, respectively.

Temperature (K)	$M_{\text{Fe-16d}}$ ($\mu_{\text{B}}/\text{atom}$) ($T_{\text{A}} \sim 1473\text{K}$)	$M_{\text{Fe-16d}}$ ($\mu_{\text{B}}/\text{atom}$) ($T_{\text{A}} \sim 1073\text{K}$)	$M_{\text{Fe-6h}}$ ($\mu_{\text{B}}/\text{atom}$) ($T_{\text{A}} \sim 1073\text{K}$)	$M_{\text{Fe-2a}}$ ($\mu_{\text{B}}/\text{atom}$) ($T_{\text{A}} \sim 1073\text{K}$)
10	1.70(3)	1.67(2)	0.69(3)	0
30	1.70(3)	1.67(3)	0.68(3)	0
50	1.70(3)	1.67(3)	0.70(4)	0
70	1.70(3)	1.66(2)	0.68(4)	0
90	1.69(3)	1.65(2)	0.69(3)	0
110	1.68(3)	1.64(2)	0.66(3)	0
130	1.67(3)	1.63(2)	0.66(4)	0
150	1.64(3)	1.63(3)	0.64(3)	0
170	1.63(3)	1.61(3)	0.60(4)	0
190	1.62(4)	1.59(3)	0.59(4)	0
210	1.58(3)	1.56(2)	0.55(4)	0
230	1.54(4)	1.50(2)	0.52(5)	0
250	1.49(3)	1.45(3)	0.49(5)	0
270	1.44(4)	1.39(3)	0.44(6)	0
290	1.37(3)	1.30(2)	0.36(6)	0
310	1.27(3)	1.23(2)	0.36(7)	0
330	1.11(3)	1.07(2)	0.25(9)	0
350	0.92(3)	0.95(2)	0.17(4)	0
370	0.81(3)	0.80(1)	0	0
390	0.60(3)	0.65(2)	0	0
410	0.40(3)	0.48(2)	0	0
430	0.18(3)	0.25(2)	0	0
450	0	0	0	0

Table S5. Temperature dependence of lattice parameters for cubic symmetry determined by NPD patterns for $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compounds with $T_A \sim 1473$ K and 1073 K (10–530 K).

Lattice parameter	a (Å) ($T_A \sim 1473\text{K}$)	unit cell volume (Å ³)	a (Å) ($T_A \sim 1073\text{K}$)	unit cell volume (Å ³)
10	6.9942(3)	342.140(6)	6.9968(2)	342.527(0)
30	6.9942(1)	342.141(0)	6.9967(2)	342.513(0)
50	6.9942(1)	342.140(0)	6.9967(2)	342.520(0)
70	6.9942(1)	342.154(9)	6.9968(2)	342.533(0)
90	6.9944(1)	342.176(9)	6.9972(2)	342.581(0)
110	6.9947(1)	342.227(9)	6.9974(2)	342.617(0)
130	6.9950(1)	342.266(9)	6.9979(2)	342.695(0)
150	6.9955(1)	342.334(9)	6.9984(2)	342.770(0)
170	6.9958(1)	342.389(9)	6.9989(2)	342.837(0)
190	6.9962(1)	342.445(0)	6.9994(2)	342.907(0)
210	6.9969(1)	342.482(0)	6.9999(2)	342.990(9)
230	6.9971(1)	342.539(0)	7.0003(2)	343.047(0)
250	6.9973(1)	342.569(0)	7.0008(2)	343.113(9)
270	6.9974(1)	342.600(0)	7.0013(2)	343.185(9)
290	6.9976(1)	342.624(0)	7.0015(2)	343.220(9)
310	6.9976(1)	342.643(0)	7.0023(2)	343.344(9)
330	6.9975(1)	342.646(0)	7.0027(2)	343.403(8)
350	6.9975(1)	342.635(0)	7.0028(2)	343.417(8)
370	6.9973(1)	342.631(0)	7.0026(2)	343.388(9)
390	6.9972(1)	342.608(0)	7.0026(2)	343.387(9)
410	6.9972(1)	342.594(0)	7.0022(2)	343.326(9)
430	6.9970(1)	342.559(0)	7.0018(2)	343.262(8)
450	6.9970(1)	342.558(0)	7.0015(2)	343.226(8)
470	6.9971(1)	342.578(0)	7.0018(2)	343.260(8)
490	6.9976(1)	342.646(0)	7.0021(2)	343.309(8)
510	6.9984(1)	343.768(0)	7.0029(2)	343.432(8)
530	6.9995(1)	342.922(0)	7.0039(2)	343.576(8)

Table S6. Temperature dependence of lattice parameters for hexagonal symmetry determined by NPD patterns for $\text{Zr}_{0.7}\text{Ta}_{0.3}\text{Fe}_2$ compound with $T_A \sim 1073$ K (10–530 K).

Lattice parameter	a (Å)	c (Å)	unit cell volume (Å ³)
10	4.9118(2)	8.0474(5)	168.138(3)
30	4.9118(2)	8.0472(5)	168.134(3)
50	4.9118(2)	8.0473(4)	168.139(3)
70	4.9120(1)	8.0475(5)	168.156(3)
90	4.9125(1)	8.0478(4)	168.198(3)
110	4.9130(2)	8.0479(5)	168.229(3)
130	4.9137(2)	8.0483(4)	168.291(3)
150	4.9145(2)	8.0489(5)	168.352(3)
170	4.9153(2)	8.0490(4)	168.410(3)
190	4.9161(2)	8.0494(4)	168.472(3)
210	4.9170(2)	8.0496(5)	168.541(3)
230	4.9180(2)	8.0496(5)	168.606(3)
250	4.9189(2)	8.0502(5)	168.682(3)
270	4.9201(2)	8.0504(5)	168.767(3)
290	4.9210(2)	8.0511(4)	168.834(2)
310	4.9225(2)	8.0517(4)	168.951(2)
330	4.9237(1)	8.0515(4)	169.045(2)
350	4.9249(1)	8.0514(4)	169.124(2)
370	4.9258(2)	8.0525(5)	169.180(2)
390	4.9267(1)	8.0533(4)	169.269(3)
410	4.9276(2)	8.0541(4)	169.343(3)
430	4.9283(2)	8.0549(4)	169.410(2)
450	4.9293(1)	8.0565(5)	169.500(3)
470	4.9303(1)	8.0577(4)	169.599(3)
490	4.9312(1)	8.0591(4)	169.687(2)
510	4.9324(2)	8.0603(4)	169.794(2)
530	4.9335(2)	8.0613(4)	169.898(2)

Theoretical calculations on kagomé (Zr_{0.7}Ta_{0.3})Fe₂

Magnetism in C14 structure.

Despite of the experimental evidence that Fe on 2a site have no ordered magnetic moments in the AFM state down to 10 K, our ab-initio electronic structure calculations in Disordered Local Moment formalism show that in high temperature paramagnetic state the Fe sites on 2a positions develop a stable local moment at about 1.16 μ_B /atom. Its magnitude is quite a similar to the Fe (6h) in kagomé plane (1.39 μ_B /atom). The absence of the order on 2a positions at low temperatures has a reason in the inter-plane magnetic frustration.

In order to elucidate the frustration of magnetic interactions in C14 structure that lead to the ordered magnetic state, where Fe on 6h position form an AFM structure of the altered FM kagomé planes, and Fe on 2a positions remain disordered down to 10 K, we calculate the interatomic exchange interactions between Fe magnetic moments in DLM state. To this end we use the first-principles magnetic force theorem (MFT) based on the Green function formalism⁵ implemented in KKR ASA⁶ to calculate the exchange constants of the classical Heisenberg Hamiltonian:

$$H_{cl} = - \sum_{i,j} J_{ij} \vec{e}_i \cdot \vec{e}_j, \quad (1)$$

where $\vec{e}_i$ is a directional unit vector of the magnetic spin moment at the i^{th} lattice site. The calculations has been performed for 12 nearest neighbor shells of each Fe positions (2a and 6h). These interactions are divided into three categories: inter-sublattices 2a-6h and intra-sub lattices 2a-2a and 6h-6h interactions, and considering (111) planes – there is interplane and intra=plane interactions of each kind. The calculated values are given in the Table I. The positive sign of the J_{ij} is FM interaction and negative is AFM (see equ.1).

Table S7. Calculated inter-atomic exchange interactions. Numbers in bracket –number of nearest neighbors (NN) of the first-site in corresponding shell. “inter” and “intra” mark inter-plane and intra-plane exchanges with respect of the planes parallel to kagomé (see figure 2). 2nd plane note – mark the interactions between 2nd NN planes.

Shell	J_{ij} (2a-2a), mRy	J_{ij} (2a-6h), mRy	J_{ij} (6h-6h), mRy
1NN	-0.047 (2) inter	0.437 (6)	1.195 (2) intra
2NN	-0.110 (6) intra	-0.073 (12)	0.659 (2) intra
3NN	0.009 (12) inter	-0.080 (12)	-0.003 (4) intra
4NN	-0.001 (2) inter	-0.034 (6) 2 nd plane	-0.024 (4) inter
5NN		-0.019 (12)	-0.169 (4) inter
6NN		-0.009 (12) 2 nd plane	0.275 (6) intra
7NN		-0.015 (6)	0.514 (2) inter
8NN		-0.006 (12) 2 nd plane	-0.077 (8) inter

Spontaneous volume magnetostriction based on experimental data

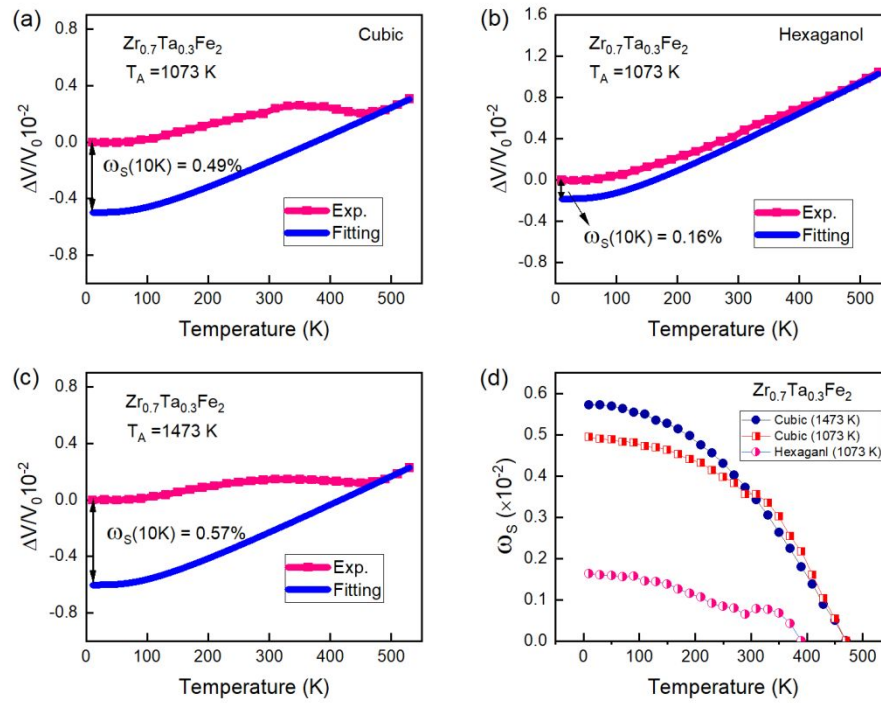


Figure S7. The Fitting curves of unit cell volume and temperature dependence of spontaneous volume magnetostriction (ω_s) for $Zr_{0.7}Ta_{0.3}Fe_2$ compounds with $T_A \sim 1473$ K and 1073K, respectively.

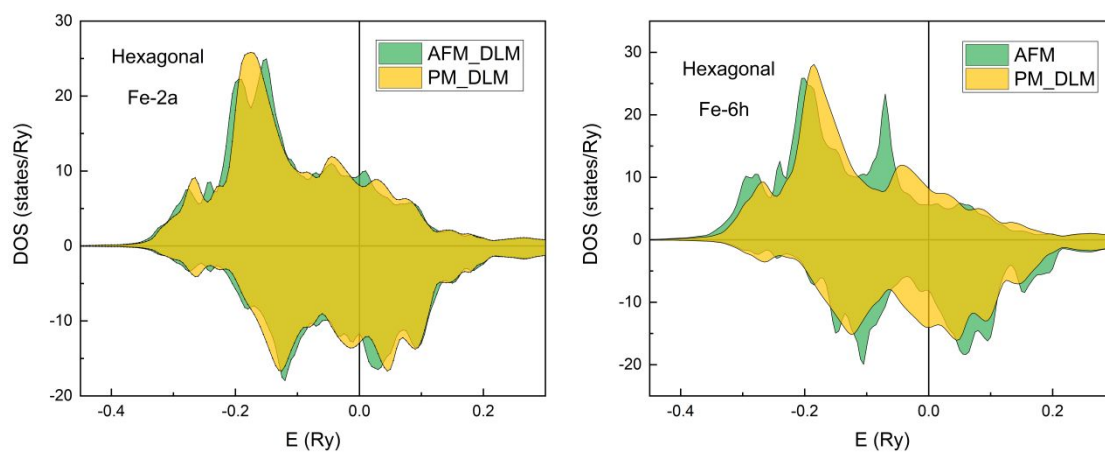


Figure S8. Atomic resolved contribution to Density of State (DOS) patterns of Fe at 2a and 6h atomic sites for hexagonal $(\text{Zr}_{0.7}\text{Ta}_{0.3})\text{Fe}_2$ compounds.

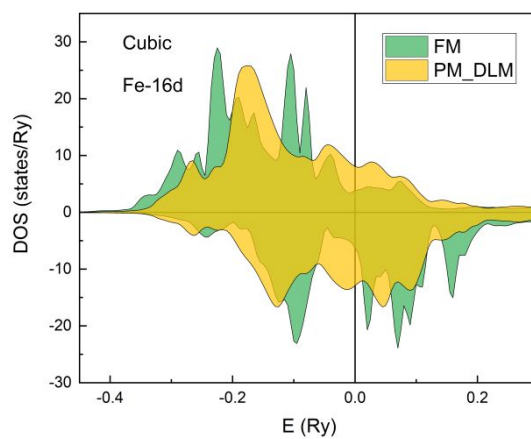


Figure S9. Atomic resolved contribution to Density of State (DOS) patterns of Fe at 16d atomic sites for cubic $(\text{Zr}_{0.7}\text{Ta}_{0.3})\text{Fe}_2$ compounds.

References

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- [1] (a) G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); (b) G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
 - [2] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
 - [3] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [4] B. Delley, *J. Chem. Phys.* **92**, 508 (1990).
 - [5] A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, *J. Magn. Magn. Mater.* **67**, 65 (1987).
 - [6] A. V. Ruban, S. I. Simak, S. Shallcross, and H. Skriver, *Phys. Rev. B* **67**, 214302 (2003).