

Ab initio methods in solid state physics

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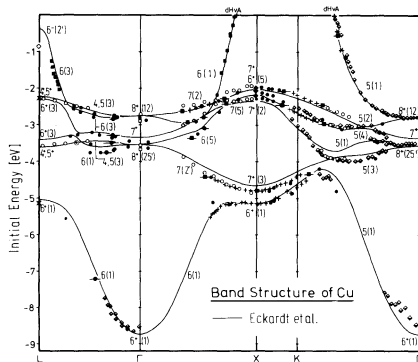
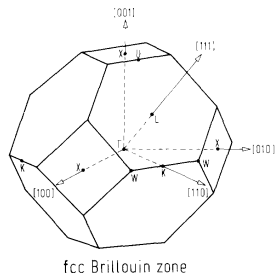
March 25, 2021

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Band structure of Cu – comparison with experiment

Band structure of copper obtained from the angle resolved photoemission spectroscopy (ARPES) and DFT calculations, $E < E_F$.

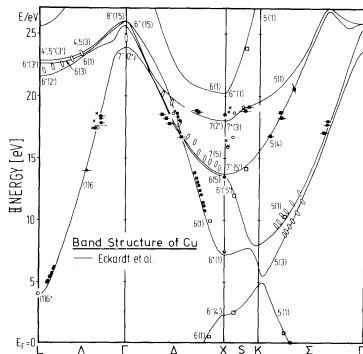
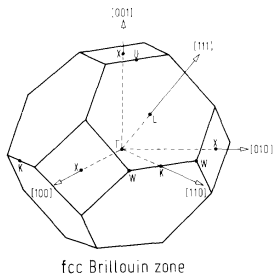


R. Courths and S. Hufner, Phys. Rep. **112**, 53 (1984).

H. Eckardt, L. Fritsche, and J. Noffke, J. Phys. F: Met. Phys. **14**, 97 (1984).

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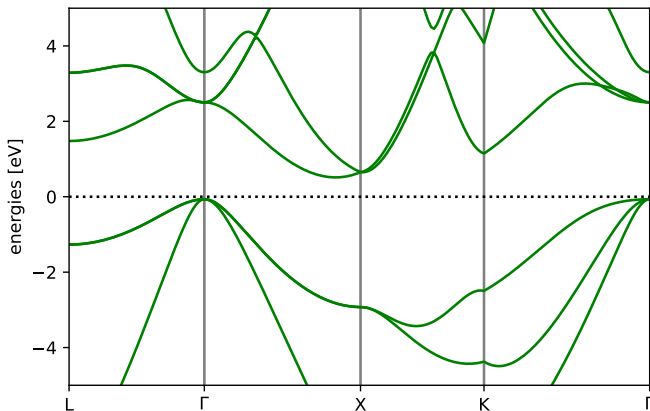


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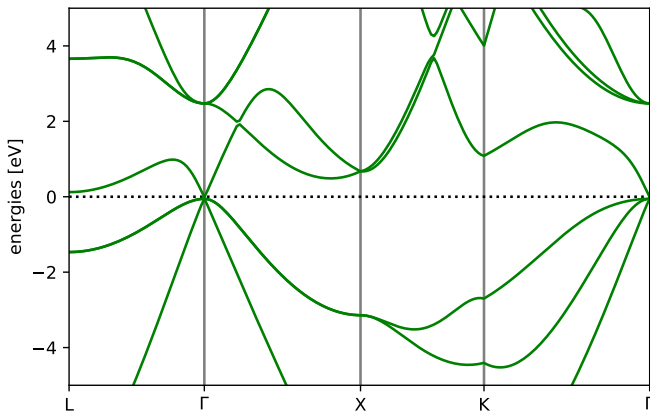
Band structure of Si

Calculations for silicon gives the energy gap $E_g = 0.58$ eV (GGA-PBE), which is underestimated by $\sim 50\%$ comparing to the experimental value $E_g^{\text{exp}} = 1.14$ eV.

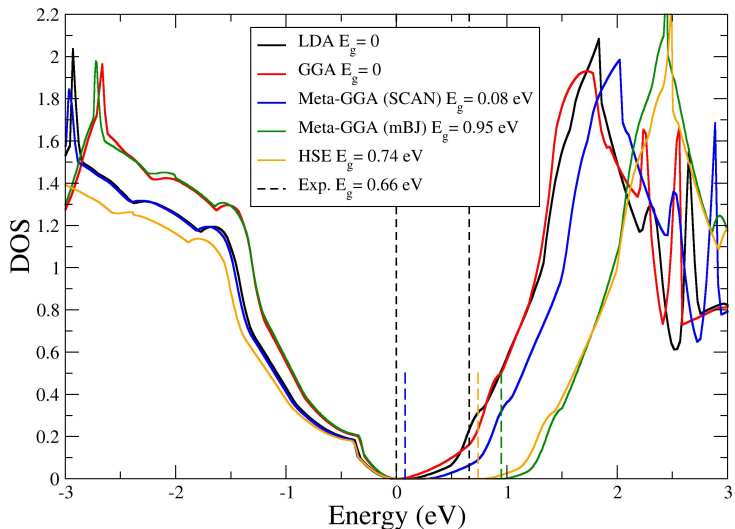


Band structure of Ge

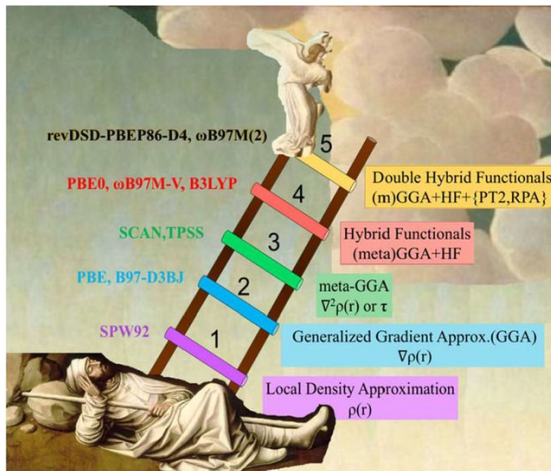
Calculations for germanium, which is a semiconductor with the energy gap $E_g^{\text{exp}} = 0.66$ eV, gives the metallic state (in LDA or GGA).



Electronic density of states of Ge



Jacob's ladder of DFT



J. M. L. Martin and G. Santra, IJC **60**, 787 (2020).

Energy gap problem

The fundamental energy gap can be obtained as the difference between the first ionization energy I and the first electron affinity A of the neutral solid

$$I = E(N - 1) - E(N), \quad (1)$$

$$A = E(N) - E(N + 1), \quad (2)$$

$$E_g = I - A = [E(N - 1) - E(N)] - [E(N) - E(N + 1)], \quad (3)$$

$$\begin{aligned} E_g &= E(N + 1) - E(N) - [E(N) - E(N - 1)] = \varepsilon_{N+1}(N + 1) - \varepsilon_N(N) \\ &= \varepsilon_{N+1}(N) - \varepsilon_N(N) + \varepsilon_{N+1}(N + 1) - \varepsilon_{N+1}(N) = \Delta_{\text{KS}} + \Delta_{\text{xc}}. \end{aligned} \quad (4)$$

Kohn-Sham energy gap

$$\Delta_{\text{KS}} = \varepsilon_{N+1}(N) - \varepsilon_N(N), \quad (5)$$

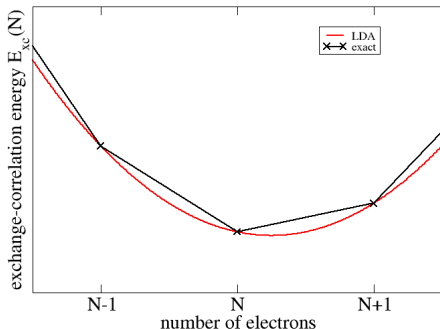
$\varepsilon_{N+1}(N)$ – lowest unoccupied KS state,

$\varepsilon_N(N)$ – highest occupied KS state.

Energy gap problem

Derivative of the exchange-correlation functional is discontinuous with the change of number of electrons – this effect is not described by analytical functionals.

$$\Delta_{xc} = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \Big|_{N+\delta} - \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \Big|_{N-\delta} = 0 \quad (\text{LDA, GGA}) \quad (6)$$



Exchange charge density

A. D. Becke, Int. J. Quantum Chem. **23**, 1915 (1983).

The exchange energy can be written using the spin density matrix

$$E_x = -\frac{1}{2} \sum_{\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{|\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (7)$$

$$\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \psi_i^{\sigma*}(\mathbf{r}_1) \psi_i^{\sigma}(\mathbf{r}_2). \quad (8)$$

Exchange charge density with respect to the reference point \mathbf{r}

$$\rho_{x\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s}) = \frac{|\rho_{\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s})|^2}{n_{\sigma}(\mathbf{r})}, \quad \mathbf{r} = \mathbf{r}_1, \quad \mathbf{s} = \mathbf{r}_2 - \mathbf{r}_1. \quad (9)$$

Taylor expansion of the exact spherically averaged exchange charge density

$$\rho_{x\sigma}(\mathbf{r}, s) = n_{\sigma}(\mathbf{r}) + \frac{1}{6} [\nabla^2 n_{\sigma}(\mathbf{r}) - 2\tau_{\sigma}(\mathbf{r}) + \frac{1}{2} \frac{(\nabla n_{\sigma}(\mathbf{r}))^2}{n_{\sigma}(\mathbf{r})}] s^2 + \dots, \quad (10)$$

$$\tau_{\sigma}(\mathbf{r}) = \sum_i |\nabla \psi_{i\sigma}(\mathbf{r})|^2. \quad (11)$$

A. D. Becke and E. R. Johnson, J. Chem. Phys. **124**, 221101 (2006)

$$V_{x\sigma}^{\text{BJ}}(\mathbf{r}) = V_{x\sigma}^{\text{Slater}}(\mathbf{r}) + \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2\tau_{\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})}}, \quad (12)$$

$$V_{x\sigma}^{\text{Slater}}(\mathbf{r}) = -\frac{1}{2} \int d\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (13)$$

F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)

modified Becke-Johnson potential

$$V_{x\sigma}^{\text{mBJ}}(\mathbf{r}) = cV_{x\sigma}^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2\tau_{\sigma}(\mathbf{r})}{n_{\sigma}(\mathbf{r})}}, \quad (14)$$

$$V_{x\sigma}^{\text{BR}}(\mathbf{r}) = -\frac{1}{b_{\sigma}(\mathbf{r})} (1 - e^{-x_{\sigma}(\mathbf{r})} - \frac{1}{2} x_{\sigma}(\mathbf{r}) e^{-x_{\sigma}(\mathbf{r})}). \quad (15)$$

Electron localization function (ELF)

Meta-GGA functionals use the dimensionless parameter

$$\alpha = \frac{\tau - \tau^w}{\tau^u}, \quad (16)$$

where τ^w is the Weizsäcker density of kinetic energy $\tau^w = |\nabla n|^2/8n$, which defines τ for a single orbital, and τ^u is the value for a uniform gas

$$\tau^u = \frac{3}{10} \left(\frac{3}{\pi^2} \right)^{\frac{2}{3}} n^{\frac{5}{3}}. \quad (17)$$

Parameter $\alpha \in [0, 1]$ is connected with the electron localization function

$$\text{ELF} = \frac{1}{1 + \alpha^2}, \quad (18)$$

which is used to characterize the distribution of electron density

- ❶ slowly changing density, typical for metals, $\alpha \approx 1$, $\text{ELF} \approx \frac{1}{2}$.
- ❷ covalent bonds between two orbitals, $\alpha = 0$, $\text{ELF} = 1$.
- ❸ weak noncovalent bonds between closed atomic shells, $\alpha \rightarrow \infty$, $\text{ELF} \rightarrow 0$.

Meta-GGA functionals

The exchange-correlation functional in meta-GGA is written in a general form

$$E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{xc}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}). \quad (19)$$

J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015).

Strongly constrained and appropriately normed (SCAN) functional obeys all 17 known exact constraints. The exchange part can be written in a form

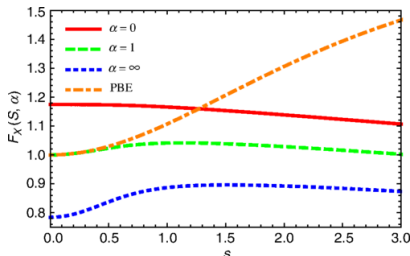
$$E_{\text{x}}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{\text{x}}(n) F_{\text{x}}(s, \alpha), \quad (20)$$

where $\varepsilon_{\text{x}}(n)$ is the exchange energy for uniform gas per one electron and s is the dimensionless gradient of density

$$s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}. \quad (21)$$

Meta-GGA functionals

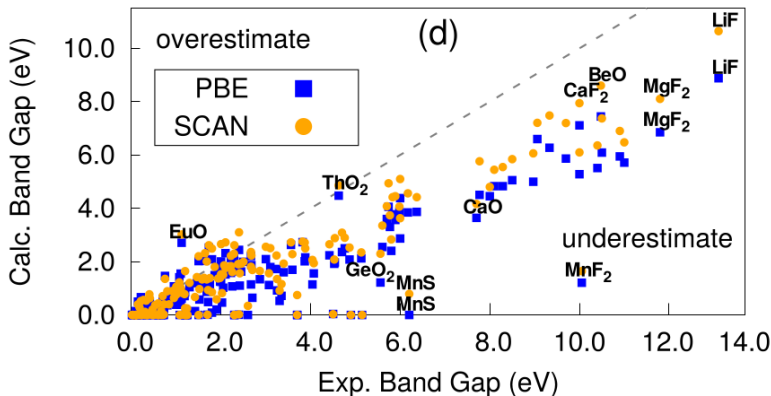
In this figure, F_x is plotted as a function of s for three characteristic values of α . F_x fulfills the condition for $s \rightarrow 0$, as well as for $s \rightarrow \infty$. For $\alpha = 1$ and small s , F_x coincides with the GGA-PBE functional. Values of F_x for other values of α are obtained using the interpolation between $\alpha = 0$ and $\alpha = 1$, and the extrapolation for $\alpha \rightarrow \infty$.



The full exchange-correlation function $F_{xc} = F_x + F_c$, in the limit of high density, converges to F_x , while for small density it fulfills the Lieb-Oxford bound, $F_{xc} \leq 2.215$.

Meta-GGA functionals

E. B. Isaacs and C. Wolverton, Phys. Rev. Mater. **2**, 063801 (2018)



Self-interaction problem

One electron system - hydrogen atom ($E = E_k + E_Z$)

LDA or GGA

E_H - exact, E_x , E_c - approximate

$E_H \neq E_x + E_c \rightarrow E_H + E_x + E_c \neq 0$ (self-interaction)

Hartree-Fock

$$\begin{aligned} E_x &= -\frac{1}{2} \sum_{i=j,\sigma} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\psi_i^{\sigma*}(\mathbf{r}_1) \psi_j^{\sigma*}(\mathbf{r}_2) \psi_i^{\sigma}(\mathbf{r}_2) \psi_j^{\sigma}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= -\frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} = -E_H \end{aligned} \quad (22)$$

$\rightarrow E_H + E_x = 0$ (no self-interaction)

Hybrid functionals

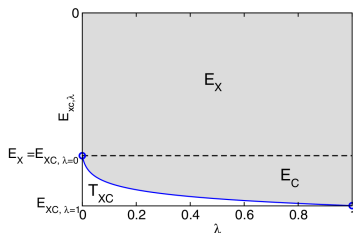
A. D. Becke, J. Chem. Phys. **98**, 1372 (1993)

$$H_\lambda = E_k + \lambda V \quad \frac{dE_\lambda}{d\lambda} = \langle \psi_\lambda | V | \psi_\lambda \rangle. \quad (23)$$

Adiabatic connection formula

$$E[n] = E_k[n] + \int_0^1 d\lambda \langle \psi_\lambda | V | \psi_\lambda \rangle, \quad (24)$$

$$E_{xc}[n] = \int_0^1 d\lambda \langle \psi_\lambda | V | \psi_\lambda \rangle - E_H[n] = \int_0^1 d\lambda E_{xc,\lambda}[n], \quad (25)$$



$$E_{xc,\lambda}[n] = (1 - \lambda)E_x^{\text{HF}}[n] + \lambda E_{xc}^{\text{DFT}}[n], \quad (26)$$

$$E_{xc}^{\text{hyb}}[n] = \frac{1}{2}E_x^{\text{HF}}[n] + \frac{1}{2}E_{xc}^{\text{DFT}}[n]. \quad (27)$$

J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996)

$$E_{xc}^{hyb}[n] = E_{xc}^{DFT}[n] + \alpha(E_x^{HF}[n] - E_x^{DFT}[n]), \quad (28)$$

$$\alpha = 0.25 \text{ (PBE0)},$$

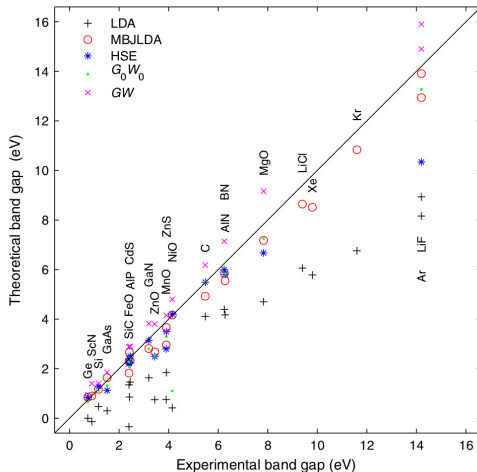
$$\alpha = 0.5 \text{ (Fock-0.5)}.$$

J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003)
(HSE)

$$E_{xc}^{hyb}(\mu) = (1 - \alpha)E_x^{GGA,SR}(\mu) + \alpha E_x^{HF,SR}(\mu) + E_x^{GGA,LR} + E_c^{GGA}. \quad (29)$$

Meta-GGA potential mBJ vs functional HSE

Solid	LDA	MBJLDA	HSE	G_0W_0	GW	Expt.
Ne (A1)	11.42	22.72		19.59 ^e	22.1 ^g	21.70
Ar (A1)	8.16	13.91	10.34 ^a	13.28 ^e	14.9 ^g	14.20
Kr (A1)	6.76	10.83				11.6
Xe (A1)	5.78	8.52				9.8
C (A4)	4.11	4.93	5.49 ^b	5.50 ^e	6.18 ^g	5.48
Si (A4)	0.47	1.17	1.28 ^b	1.12 ^e	1.41 ^g	1.17
Ge (A4)	0.00	0.85	0.83 ^b	0.66 ^f	0.95 ^g	0.74
LiF (B1)	8.94	12.94		13.27 ^e	15.9 ^g	14.20
LiCl (B1)	6.06	8.64				9.4
MgO (B1)	4.70	7.17	6.67 ^b	7.25 ^e	9.16 ^g	7.83
ScN (B1)	-0.14	0.90		0.95 ^f	1.4 ^h	~0.9
MnO (B1)	0.76	2.95	2.8 ^c		3.5 ⁱ	3.9 ± 0.4
FeO (B1)	-0.35	1.82	2.2 ^c			2.4
NiO (B1)	0.42	4.16	4.2 ^c	1.1 ^f	4.8 ⁱ	4.0, 4.3
SiC (B3)	1.35	2.28	2.40 ^b	2.27 ^e	2.88 ^g	2.40
BN (B3)	4.39	5.85	5.99 ^b	6.10 ^e	7.14 ^g	~6.25
GaN (B3)	1.63	2.81	3.14 ^b	2.80 ^e	3.82 ^g	3.20
GaAs (B3)	0.30	1.64	1.12 ^b	1.30 ^e	1.85 ^g	1.52
AlP (B3)	1.46	2.32	2.51 ^b	2.44 ^e	2.90 ^g	2.45
ZnS (B3)	1.84	3.66	3.49 ^b	3.29 ^e	4.15 ^g	3.91
CdS (B3)	0.86	2.66	2.25 ^b	2.06 ^e	2.87 ^g	2.42
AlN (B4)	4.17	5.55	5.81 ^b	5.83 ^f		6.28
ZnO (B4)	0.75	2.68	2.49 ^d	2.51 ^f	3.8 ^g	3.44



J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein and J. P. Perdew, *Nature Chemistry* **8**, 831 (2016)

Table 2 | Properties of prototypical ferroelectric (BaTiO₃ and PbTiO₃) and multiferroic (BiFeO₃) materials predicted by LDA, PBE with and without the Hubbard U correction, SCAN and hybrid GGAs.

System	Property	LDA	PBE (U = 2)	HSE	SCAN	B1WC	Expt
BaTiO ₃	E_g	1.72	1.73	3.27	2.13	3.44	3.38
	V_0	62.1	67.5	64.5	65.1	63.2	64.0
	c/a	1.011	1.054	1.039	1.029	1.015	1.010
	P_s	0.24	0.47	0.41	0.35	0.28	0.27
	ΔE	5.0	56.1	53.8	25.1	24	-
	μ	1.47	1.88	3.00	2.08	2.83	3.60
PbTiO ₃	E_g	60.4	70.4	65.2	64.9	62.4	62.6
	V_0	1.045	1.239	1.158	1.122	1.097	1.071
	c/a	1.045	1.239	1.158	1.122	1.097	1.071
	P_s	0.80	1.26	1.14	1.06	1.03	~0.5 - 1.00
	ΔE	58.1	204.8	194.1	122.7	110.6	-
	μ	0.34	1.05 (1.76)	3.4	1.89	3.0	2.74
BiFeO ₃	V_0	345.1	382.7 (384.8)	375.1	369.8	369.0	373.9
	P_s	0.989	1.048 (1.003)	1.103	1.027	-	1.0
	μ	3.27	3.70 (3.95)	4.1	3.96	4.2	3.75

In the PBE column, the values of PBE with $U = 2$ correction are in parentheses. The B1WC hybrid GGA³⁷ designed for ferroelectric materials is used as the reference in the second last columns. E_g (eV) is the fundamental bandgap, V_0 (Å³) is the volume, c/a is the ratio of the lattice constants c and a , and P_s (C m⁻²) is the polarization of the tetragonal phases. ΔE (meV per cell) is the total energy difference between the cubic and tetragonal phases. μ (μ_B) is the magnetic moment per Fe. The B1WC and experimental results for BaTiO₃ and PbTiO₃ are from ref. 37, and the hybrid GGAs and experimental results for BiFeO₃ are from ref. 38. The experimental polarization for BiFeO₃ is taken from ref. 52.

Ag₂ZnSnSe₄ and Cu₂ZnSnSe₄

D. Fritsch and S. Schorr, J. Phys. Energy **3**, 015002 (2021)

