

Numerical Quality Control for DFT-based Materials Databases

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I. SUPPLEMENTARY METHODS

A. General, Code-independent Details

In Kohn-Sham (KS) density-functional theory (DFT), the electronic many-body Schrödinger equation is recast as a set of independent particle equations, the Kohn-Sham equations¹

$$\underbrace{[\hat{t} + v_{\text{ext}} + v_{\text{H}} + v_{\text{XC}}]}_{h_{\text{KS}}} \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) , \quad (1)$$

which are solved in all codes discussed in this manuscript to determine the electronic Kohn-Sham (KS) eigenvalues ϵ_i and eigenstates $\psi_i(\mathbf{r})$. In Equation (1), $\hat{t}$ is the kinetic energy operator, v_{ext} denotes the external electrostatic potential stemming from the N -nuclei (position $\mathbf{R}_I$, charge Z_I), the Hartree potential v_{H} describes the electrostatic interactions between the electrons in the mean-field approximation, and the exchange-correlation (XC) potential v_{XC} subsumes all many-body effects beyond the classical mean-field interactions. In this work, two approximations were used to capture the XC effects: the local-density approximation (LDA) in the parameterization proposed by Perdew and Wang^{2,3} and PBE⁴ as a representative example for the generalized gradient approximation (GGA). Since both v_{H} and v_{XC} depend on the electron density $n(\mathbf{r})$, which is in turn determined by the occupied KS states, the KS equations are solved iteratively, until self-consistency is reached.

Crystalline materials are treated by using periodic boundary conditions to account for the translational symmetry determined by the lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. Accordingly, the KS states have to fulfill Bloch's theorem and become continuous functions of the wavevector $\mathbf{k}$, and so do the KS Hamiltonian $h_{\text{KS}}(\mathbf{k})$ and the eigenvalues $\epsilon_i(\mathbf{k})$. Integrals $\int d\mathbf{k}$ over the Brillouin zone, as spanned by the primitive reciprocal space vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, are approximated in the codes employed in this paper by sums over a finite grid of $\mathbf{k}$ -points. We have chosen a Γ -centered $q_1 \times q_2 \times q_3$ grid defined via

$$\mathbf{k} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \text{ with } m_r = \frac{n - q_r}{q_r} \quad (2)$$

and $n \in [0, q_r]$ in all cases. For odd values of q_r , these correspond to Monkhorst-Pack type grids. To investigate convergence with respect to this numerical setting, three different $\mathbf{k}$ -point densities were investigated, which correspond to 2, 4, and 8 pt. per $\text{\AA}^{-1}$ along each primitive reciprocal space vector. The $\mathbf{k}$ -point density $\rho^{\mathbf{k}}$ is defined as:

$$\rho_i^{\mathbf{k}} = N_i^{\mathbf{k}} / |\mathbf{G}_i|, \quad \text{with } i = x, y, z, \quad (3)$$

N_i^k is the number of $\mathbf{k}$ -points and $\mathbf{G}_i$ the reciprocal lattice vector for direction $i = x, y, z$.

Accordingly, the electron density is given by

$$n(\mathbf{r}) = \sum_{\mathbf{k}} \sum_i f(\epsilon_i(\mathbf{k})) |\psi_i(\mathbf{k}, \mathbf{r})|^2, \quad (4)$$

where the $f(\epsilon_i(\mathbf{k}))$ are the occupation numbers. In this work, the $f(\epsilon_i(\mathbf{k}))$ are calculated using a Fermi smearing

$$f(\epsilon_i(\mathbf{k})) = \frac{1}{1 + \exp[(\epsilon_i(\mathbf{k}) - \epsilon_F)/\beta]} \quad (5)$$

with a smearing width of $\beta = 100$ meV and a Fermi energy ϵ_F that is implicitly defined via

$$\sum_{i, \mathbf{k}} f(\epsilon_i(\mathbf{k})) = N_e, \quad (6)$$

in which N_e is the number of electrons. This ‘smearing out’ ensures numerical stability in the self-consistency cycle whenever (virtually) degenerate states are present.

The total energy of the combined electronic-nuclear system for a fixed nuclear geometry is thereby given via

$$E_{\text{tot}} = \frac{1}{2} \sum_{i, \mathbf{k}} f(\epsilon_i(\mathbf{k})) |\nabla \psi_i|^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \int \left(v_{\text{ext}} + \frac{1}{2} v_{\text{H}} \right) n(\mathbf{r}) d\mathbf{r} + E_{\text{XC}}[n]. \quad (7)$$

The last term denotes the XC energy, which is related to the associated XC potential via the functional derivative

$$v_{\text{XC}}(\mathbf{r}) = \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})}. \quad (8)$$

Note that `exciting` and `FHI-aims` use the expression

$$E_{\text{tot}} = \sum_{i, \mathbf{k}} f(\epsilon_i(\mathbf{k})) \epsilon_i(\mathbf{k}) + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{1}{2} \int v_{\text{H}} n(\mathbf{r}) d\mathbf{r} - \int (v_{\text{XC}} - \epsilon_{\text{XC}}) n(\mathbf{r}) d\mathbf{r} \quad (9)$$

that is equivalent to Equation (7) when self-consistency is achieved. Last but not least, let us note that the discussed formalism does not only allow for computing the total energy of the combined electronic-nuclear system defined in Equation (7), but also its analytical derivatives with respect to the nuclear positions, e.g, forces

$$\mathbf{F}_I = -\nabla_{\mathbf{R}_I} E_{\text{tot}} \quad (10)$$

associated to changes in the atomic coordinates $\mathbf{R}_I$. In this work, these forces are also used to monitor the degree of convergence during the self-consistency cycle, see Tab. I.

Physical property	Break condition		
	exciting	FHI-aims	GPAW
Electron density:	$0.1 \mu e^a$	$10 \mu e^b$	$100 \mu e/\text{electron}^a$
Total energy Eq. (7): $E_{\text{tot}}^\nu - E_{\text{tot}}^{\nu-1}$	$2.7 \mu eV$	$10 \mu eV$	$500 \mu eV$
Eigenvalues: $\sum_i [f(\epsilon_i^\nu)\epsilon_i^\nu - f(\epsilon_i^{\nu-1})\epsilon_i^{\nu-1}]$	n/a	$10 \mu eV$	n/a
Maximum force on atoms (Eq. (10)): $[\max(F_{\text{at}}^I)]^\nu - [\max(F_{\text{at}}^I)]^{\nu-1}$	n/a	$0.1 \text{ meV}/\text{\AA}$	$2.0 \text{ meV}/\text{\AA}$

^a GPAW, exciting: $\int |n^\nu(\mathbf{r}) - n^{\nu-1}(\mathbf{r})| d\mathbf{r}$

^b FHI-aims: $\sqrt{\int |n^\nu(\mathbf{r}) - n^{\nu-1}(\mathbf{r})|^2 d\mathbf{r}}$

TABLE I. Convergence criteria, i.e., the break conditions for the iterations ν in the self-consistency cycle.

As mentioned above, the KS equations are solved self-consistently and breaking conditions have to be defined to end this self-consistency loop. For this purpose, changes in the density, the energy, the eigenvalues, and in the forces can be monitored during the cycle. Tab. I summarizes the breaking conditions used throughout this study in the different codes, whereby not all codes allow monitoring all these quantities (independently) and not all codes use the same metrics. For this reason, extremely conservative settings were chosen for all codes, so to ensure that numerical uncertainties in the total energy stemming from this breaking conditions are much smaller than 10^{-5} eV.

B. Code-Dependent Considerations

In practice, all implementations of DFT discussed in this work expand the KS states

$$\psi_l(\mathbf{r}, \mathbf{k}) = \sum_{i=1}^{N_b} c_{il}(\mathbf{k}) \chi_i(\mathbf{r}, \mathbf{k}) \quad (11)$$

in a finite basis set $\chi_i(\mathbf{r}, \mathbf{k})$, so that the KS Equations (1) become a discretized, generalized eigenvalue problem

$$\sum_j h_{ij}(\mathbf{k}) c_{jl}(\mathbf{k}) = \epsilon_l(\mathbf{k}) \sum_j s_{ij}(\mathbf{k}) c_{jl}(\mathbf{k}) , \quad (12)$$

depending on the Hamiltonian and the overlap matrix:

$$h_{ij}(\mathbf{k}) = \int \chi_i^*(\mathbf{r}, \mathbf{k}) h_{\text{KS}}(\mathbf{k}) \chi_j(\mathbf{r}, \mathbf{k}) d\mathbf{r} \quad (13)$$

$$s_{ij}(\mathbf{k}) = \int \chi_i^*(\mathbf{r}, \mathbf{k}) \chi_j(\mathbf{r}, \mathbf{k}) d\mathbf{r} . \quad (14)$$

1. exciting

`exciting` follows the linearized augmented plane waves + local orbital (LAPW+LO) formalism as described in Ref. 5. The parameters used in the calculations performed in this work are summarized in Tabs. II, III, and IV. Below, we briefly explain the meaning of these parameters.

`exciting` employs two different types of basis functions. The first type, LAPWs, is defined as a plane wave that is continuously and smoothly augmented by atomic-like orbitals in non-overlapping atomic spheres (muffin tins) enclosing each nucleus. The number of LAPWs is determined by the dimensionless parameter $RK_{\max}$, where R is the radius of atomic spheres and $K_{\max}$ is the largest wave vector considered. $RK_{\max}$ describes the quality of the basis set with essentially no dependence on R . We estimate the complete-basis-set limit $E_{\text{tot}}^{\text{CBS}}$ by extrapolating the total energy to infinite $RK_{\max}$ for each material. To acquire $E_{\text{tot}}^{\text{CBS}}$, the total energy is fitted to the function

$$E_{\text{tot}}(RK_{\max}) = E_{\text{tot}}^{\text{CBS}} + ae^{-bRK_{\max}}, \quad (15)$$

where a , b , and $E_{\text{tot}}^{\text{CBS}}$ are fitting parameters. The obtained value of $E_{\text{tot}}^{\text{CBS}}$ is used to determine the $RK_{\max}$ value at which the error in the total energy is 0.1 meV/atom. This value is denoted as $RK_{\max}^{\text{opt}}$ and is listed in Tabs. II, III, and IV for each material. This parameter allows us to pick LAPW settings that guarantee comparable levels of precision in different systems.

The second type of basis functions, LOs, are defined as atomic-like orbitals within one atomic sphere and strictly zero everywhere else. In the present work, we do not explore the influence of LOs on the total energy due to the overwhelming abundance of parameters that define the variational degrees of freedom within the atomic spheres. Instead, we use a fixed well-converged configuration of LOs for each chemical species in all calculations. The number of LOs employed for each species is given in Tab. II.

Element	R [bohr]	$RK_{\max}^{\text{opt}}$	Valence shells	Numbers and types of LOs
H	0.60	5.84	1s	2 s, 2 p
He	2.10	8.23	1s	3 s, 2 p, 2 d
Li	2.10	8.45	1s 2s	4 s
Be	1.80	8.31	1s 2s	4 s, 2 p, 2 d
B	1.40	8.97	1s 2s 2p	4 s, 3 p
C	1.20	9.38	1s 2s 2p	4 s, 2 p

N	0.95	9.55	2s 2p	3 s, 3 p
O	1.05	10.24	2s 2p	3 s, 3 p, 2 d, 2 f
F	1.20	10.79	2s 2p	3 s, 3 p, 2 d, 2 f
Ne	2.50	10.44	2s 2p	3 s, 3 p, 2 d, 2 f
Na	2.10	10.64	2s 2p 3s	3 s, 2 p
Mg	2.10	10.58	2s 2p 3s	3 s, 3 p
Al	2.20	10.21	2s 2p 3s 3p	4 s, 3 p
Si	1.90	10.61	2s 2p 3s 3p	3 s, 3 p
P	1.90	10.36	2s 2p 3s 3p	4 s, 4 p, 2 d, 2 f
S	2.00	9.93	2s 2p 3s 3p	5 s, 5 p
Cl	1.70	10.22	2s 2p 3s 3p	5 s, 5 p, 2 d, 2 f
Ar	2.50	10.47	3s 3p	3 s, 3 p, 2 d, 2 f
K	2.20	10.88	3s 3p 4s	2 s, 2 p
Ca	2.10	10.77	3s 3p 4s	3 s, 3 p
Sc	2.10	11.58	3s 3p 3d 4s	3 s, 3 p, 2 d
Ti	2.10	11.80	3s 3p 3d 4s	4 s, 5 p, 3 d, 2 f, 2 g
V	2.10	11.92	3s 3p 3d 4s	3 s, 4 p, 3 d
Cr	1.90	12.26	3s 3p 3d 4s	4 s, 5 p, 3 d, 5 f, 5 g, 5 h, 5 i
Mn	1.90	12.42	3s 3p 3d 4s	4 s, 5 p, 3 d, 5 f, 5 g, 5 h, 5 i
Fe	1.90	12.57	3s 3p 3d 4s	5 s, 5 p, 3 d, 5 f, 5 g, 5 h, 5 i
Co	1.90	12.69	3s 3p 3d 4s	4 s, 5 p, 3 d, 2 f, 2 g
Ni	1.90	12.78	3s 3p 3d 4s	4 s, 4 p, 3 d, 2 f, 2 g
Cu	2.10	12.62	3s 3p 3d 4s	3 s, 4 p, 2 d
Zn	2.10	12.75	3s 3p 3d 4s	4 s, 3 p, 2 d
Ga	2.20	12.68	3s 3p 3d 4s 4p	3 s, 3 p, 2 d
Ge	2.10	12.80	3s 3p 3d 4s 4p	4 s, 4 p, 2 d
As	2.10	12.79	3s 3p 3d 4s 4p	5 s, 5 p, 3 d, 2 f, 2 g
Se	2.00	12.90	3s 3p 3d 4s 4p	5 s, 5 p, 3 d, 2 f, 2 g
Br	1.90	12.40	3p 3d 4s 4p	2 s, 4 p, 4 d, 2 f, 2 g
Kr	3.00	10.60	3p 3d 4s 4p	3 s, 5 p, 3 d, 2 f, 2 g
Rb	2.20	11.35	3s 3p 3d 4s 4p 5s	5 s, 3 p, 1 d
Sr	2.40	10.86	3d 4s 4p 5s	3 s, 2 p, 6 d
Y	2.30	11.32	3d 4s 4p 4d 5s	3 s, 3 p, 4 d
Zr	2.20	11.66	3d 4s 4p 4d 5s	2 s, 3 p, 5 d
Nb	2.20	11.86	3p 3d 4s 4p 4d 5s	4 s, 6 p, 5 d
Mo	2.10	11.89	3p 3d 4s 4p 4d 5s	2 s, 6 p, 5 d
Tc	2.10	12.31	4s 4p 4d 5s	4 s, 4 p, 3 d, 2 f, 2 g
Ru	2.10	12.55	4s 4p 4d 5s	4 s, 4 p, 3 d, 2 f, 2 g
Rh	2.10	12.74	4s 4p 4d 5s	3 s, 3 p, 2 d
Pd	2.10	12.88	4s 4p 4d	3 s, 3 p, 2 d
Ag	2.10	13.03	4s 4p 4d 5s	4 s, 3 p, 2 d
Cd	2.10	13.08	4s 4p 4d 5s	4 s, 5 p, 3 d, 2 f, 2 g
In	2.30	13.23	4s 4p 4d 5s 5p	3 s, 3 p, 3 d
Sn	2.20	13.45	4s 4p 4d 5s 5p	4 s, 4 p, 2 d
Sb	2.20	13.50	4s 4p 4d 5s 5p	4 s, 3 p, 3 d
Te	2.40	13.26	4s 4p 4d 5s 5p	4 s, 4 p, 3 d
I	2.30	13.43	4s 4p 4d 5s 5p	4 s, 3 p, 3 d

Xe	3.00	11.33	4s 4p 4d 5s 5p	5 s, 6 p, 3 d, 2 f, 2 g
Cs	2.20	13.34	4s 4p 4d 5s 5p 6s	5 s, 3 p, 3 d
Ba	2.20	13.01	4s 4p 4d 5s 5p 6s	5 s, 4 p, 4 d
Lu	2.10	15.13	4d 4f 5s 5p 5d 6s	3 s, 3 p, 3 d, 1 f
Hf	2.10	14.96	4d 4f 5s 5p 5d 6s	3 s, 3 p, 5 d, 2 f
Ta	2.10	14.61	4d 4f 5s 5p 5d 6s	4 s, 3 p, 5 d, 2 f
W	2.10	13.93	4f 5s 5p 5d 6s	5 s, 4 p, 3 d, 4 f, 2 g, 2 h
Re	2.10	13.65	4f 5s 5p 5d 6s	5 s, 4 p, 3 d, 4 f, 2 g, 2 h
Os	2.10	13.63	4f 5s 5p 5d 6s	5 s, 4 p, 3 d, 4 f, 2 g, 2 h
Ir	2.10	13.45	4f 5s 5p 5d 6s	5 s, 4 p, 3 d, 4 f, 2 g, 2 h
Pt	2.30	13.07	4d 4f 5s 5p 5d 6s	4 s, 3 p, 5 d, 3 f
Au	2.20	13.23	4d 4f 5s 5p 5d 6s	4 s, 3 p, 6 d, 5 f, 3 g, 3 h
Hg	2.30	13.26	4f 5s 5p 5d 6s	3 s, 3 p, 1 d, 3 f
Tl	2.30	13.37	4f 5s 5p 5d 6s 6p	4 s, 4 p, 2 d, 2 f
Pb	2.20	13.56	4f 5s 5p 5d 6s 6p	4 s, 4 p, 3 d, 5 f
Bi	2.20	13.57	4f 5s 5p 5d 6s 6p	4 s, 4 p, 3 d, 4 f, 2 g, 2 h
Po	2.40	13.58	4f 5s 5p 5d 6s 6p	4 s, 3 p, 3 d, 4 f
Rn	3.00	12.27	5p 5d 6s 6p	3 s, 5 p, 3 d, 2 f, 2 g

TABLE II: Computational parameters used in exciting calculations for elemental solids.

The radii of the atomic spheres chosen for elemental solids are not necessarily suitable for calculations of binary and ternary compounds. First, atomic spheres are not allowed to overlap. Second, it is likely to encounter issues due to the overcompleteness of the LAPW+LO basis in calculations where the muffin-tin radii are very different for the chemical species present in a given compound. To account for this situation, we use equal muffin-tin radii for all chemical species in a given material. The chosen radii are listed in Tabs. II, III, and IV.

To estimate the error in the total energy of binaries and ternaries, we apply Equation (3) of the main text of the paper. The model contains $\Delta E_{\text{tot},I}$ that are obtained from calculations of elemental solids. Strictly speaking, $\Delta E_{\text{tot},I}$ depends on R and RK_{max} . Our tests show that $\Delta E_{\text{tot},I}$ varies only weakly with R in the required range, thus we do not consider any dependence on this parameter. To take into account the variation with respect to RK_{max} , we use Equation 15.

Binary	R [bohr]	$RK_{\text{max}}^{\text{opt}}$	Binary	R [bohr]	$RK_{\text{max}}^{\text{opt}}$	Binary	R [bohr]	$RK_{\text{max}}^{\text{opt}}$
LiH	1.400	8.28	FeO	1.725	12.96	SnS	1.675	13.41
LiF	1.575	10.37	CoO	1.725	12.53	InSb	2.000	13.86
BeS	1.450	11.05	NiO	1.725	12.61	ZnTe	2.000	13.71
BN	1.300	9.47	CuBr	2.000	12.96	LiI	1.850	14.80

TiC	1.625	11.66	ZnO	1.725	12.50	CsCl	1.825	14.67
VN	1.725	11.78	GaP	2.000	12.66	BaO	1.825	13.74
CdO	1.725	12.61	GeTe	1.900	13.85	LuN	2.000	13.56
NaF	1.725	10.96	GaAs	2.000	13.21	HfC	1.625	14.99
NaCl	1.725	10.72	CdSe	2.000	13.34	TaC	1.625	14.95
MgO	1.725	10.96	KBr	2.100	11.85	WC	1.625	14.79
AlP	2.000	10.58	RbCl	1.825	11.96	ReO	1.725	14.18
SiC	1.625	10.93	SrO	1.825	11.54	OsB	1.725	15.01
InP	2.000	13.21	YN	1.825	11.30	IrO	1.725	13.56
ZnS	1.725	12.96	ZrC	1.625	11.65	PtO	1.725	13.78
CuCl	1.725	12.84	NbC	1.625	11.67	AuS	1.725	14.06
KCl	1.825	10.41	MoC	1.625	11.85	HgF	1.725	13.29
CaO	1.825	10.91	TcO	1.725	12.52	TlCl	1.725	14.19
ScS	1.725	11.30	RuO	1.725	11.84	PbS	1.725	13.64
TiN	1.725	11.74	RhO	1.725	12.17	BiF	1.725	13.05
VC	1.625	11.73	PdO	1.725	12.64	PoO	1.725	13.36
CrN	1.725	12.03	AgCl	1.725	12.85			
MnS	1.725	12.89	InP	2.000	13.21			

TABLE III: Computational parameters used in exciting calculations for the binary compounds considered in this work.

Ternary	R [bohr]	$RK_{\max}^{\text{opt}}$	Ternary	R [bohr]	$RK_{\max}^{\text{opt}}$
AlGaO ₃	1.70000	11.95	Li ₂ SnCl	1.71666	12.54
Ca ₂ CdP	2.06666	11.77	MgGeN ₂	1.70000	12.13
Fe ₂ NiCu	2.00000	12.35	Na ₂ IrZn	2.00000	12.61
K ₂ LiBa	2.03333	12.27	RuCO ₃	1.63333	11.42
KAgO ₃	1.88333	11.91	V ₂ CoB	1.81666	12.01

TABLE IV: Computational parameters used in exciting calculations for the ternary compounds considered in this work.

2. *FHI-aims*

Being an all-electron, full-potential code, *FHI-aims*⁶ treats all electrons on an equal footing. For this purpose, it uses real-valued, numeric atom-centered orbitals (NAOs) as a basis set:

$$\varphi_i(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\theta). \quad (16)$$

The $Y_{lm}(\theta)$ in Equation 16 are the complex spherical harmonics and $u_i(r)$ are numerically tabulated radial functions. They are chosen in order to solve a specific radial Schrödinger equation⁷ for the potential $v_i^{\text{tot}}(r) = v_i(r) + v_{\text{cut}}(r)$. In this case, $v_i(r)$ corresponds to a specific (hydrogen-, cation-, or atom-like) self-consistent potential (see Ref. 6) and thus defines the behavior of $u_i(r)$ in the proximity (up to 5-7 Å) of the nucleus. Conversely, $v_{\text{cut}}(r)$ is a steeply increasing (exponential) confining potential that is used to numerically ensure the locality of $u_i(r)$ by cutting off long-range tails. These $u_i(r)$ functions were constructed and tabulated one-by-one in a species-specific manner by systematically investigating which basis function leads to the largest improvement viz. reduction of the total energy in elemental dimers. As a starting point, the minimal basis set that solves the free-atom problem exactly was chosen⁶. For the sake of user-friendliness these $u_i(r)$ functions are grouped into tiers, so that a hierarchical pool of species-specific basis sets (‘minimal’, ‘tier 1’, ‘tier 2’, etc.) is obtained.

For crystalline materials, periodic-boundary conditions are enforced by considering all periodic images $\varphi_{i,M}(\mathbf{r}) = \varphi_i(\mathbf{r} - \mathbf{R}_I - \mathbf{T}(\mathbf{M}))$, where

$$\mathbf{R}_I + \mathbf{T}(\mathbf{M}) = \mathbf{R}_I + M_1 \mathbf{a}_1 + M_2 \mathbf{a}_2 + M_3 \mathbf{a}_3 , \quad (17)$$

includes all integer combinations of lattice vectors $\mathbf{M} = (M_1, M_2, M_3)$. This yields Bloch-type orbitals of the form

$$\chi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{M}} \exp(i\mathbf{k} \cdot \mathbf{T}(\mathbf{M})) \varphi_{i,M}(\mathbf{r}) . \quad (18)$$

By these means, all integration can be carried out in real-space over the primitive unit cell (u.c.), e.g., for the KS Hamiltonian this gives

$$h_{ij}(\mathbf{k}) = \sum_{\mathbf{M},\mathbf{N}} \exp(i\mathbf{k} [\mathbf{T}(\mathbf{N}) - \mathbf{T}(\mathbf{M})]) \int_{\text{u.c.}} \varphi_{i,M}(\mathbf{r}) h_{\text{KS}} \varphi_{j,N}(\mathbf{r}) d\mathbf{r} . \quad (19)$$

The numerical integration itself is carried out on a real-space grid (see Ref. 6 and 8–11 for details). Default settings for real space grids and cut-off potentials $v_{\text{cut}}(\mathbf{r})$ are pre-defined for each species at three levels of accuracy: ‘light’, ‘tight’, and ‘really tight’.

Beside non-relativistic calculations, FHI-aims can account for relativistic effects in two different approximations. First, the scaled zeroth order regular approximation (ZORA) is obtained by replacing the kinetic energy operator in Equation (1) by the respective ZORA operator:

$$\mathbf{p}_{\text{ZORA}} = \mathbf{p} \cdot \frac{c^2}{2c^2 - v} \cdot \mathbf{p} . \quad (20)$$

Periodic Table of Chemical Elements for Elemental Solids ^{12,13}																		18 VIIA																
1	1 194 H hP4nm		2 IIA														2 194 He hP2nm																	
2	3 166 Li hR9nm	4 194 Be hP2nm													5 166 B hR36nm	6 194 C hP4nm	7 205 N cP8nm	8 12 O mS4nm	9 15 F mS8nm	10 225 Ne cF4nm														
3	11 166 Na hR9nm	12 194 Mg hP2nm	3 IIIA		4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 225 Al cF4nm	14 227 Si cF8nm	15 64 P oS8nm	16 166 S hR3nm	17 64 Cl oS8nm	18 225 Ar cF4nm															
4	19 229 K cl2nm	20 225 Ca cF4nm	21 194 Sc hP2nm	22 194 Ti hP2nm	23 229 V cl2nm	24 229 Cr cl2nm	25 225 Mn cF4nm	26 229 Fe cl2nm	27 194 Co hP2nm	28 225 Ni cF4nm	29 225 Cu cF4nm	30 194 Zn hP2nm	31 64 Ga oS8nm	32 227 Ge cF8nm	33 166 As hR6nm	34 152 Se hP3nm	35 64 Br oS8nm	36 225 Kr cF4nm																
5	37 229 Rb cl2nm	38 225 Sr cF4nm	39 194 Y hP2nm	40 194 Zr hP2nm	41 229 Nb cl2nm	42 229 Mo cl2nm	43 194 Tc hP2nm	44 194 Ru hP2nm	45 225 Rh cF4nm	46 225 Pd cF4nm	47 225 Ag cF4nm	48 194 Cd hP2nm	49 139 In tl2nm	50 227 Sn cF8nm	51 152 Sb hR6nm	52 152 Te hP3nm	53 64 I oS8nm	54 225 Xe cF4nm																
6	55 229 Cs cl2nm	56 229 Ba cl2nm	57-71 La-Lu Lanthanide	72 194 Hf hP2nm	73 229 Ta cl2nm	74 229 W cl2nm	75 194 Re hP2nm	76 194 Os hP2nm	77 225 Ir cF4nm	78 225 Pt cF4nm	79 225 Au cF4nm	80 139 Hg tl2nm	81 194 Tl hP2nm	82 225 Pb cF4nm	83 152 Bi hR6nm	84 221 Po cP1nm	85 225 At cF4nm	86 225 Rn cF4nm																
7	87 229 Fr cl2nm	88 229 Ra cl2nm	89-103 Ac-Lr Actinide	104 Rf hP2nm	105 Db cl2nm	106 Sg cl2nm	107 Bh hP2nm	108 Hs hP2nm	109 Mt cF4nm	110 Ds cF4nm	111 Rg cF4nm	112 Uub tl2nm	113 Uut hP2nm	114 Uuq cF4nm	115 Uup hR6nm	116 Uuh cP1nm	117 Uus cF4nm	118 Uuo cF4nm																
																		155 229 Mc cl2nm	156 229 Lr cl2nm	157 Nh hP2nm	158 Db cl2nm	159 Sg cl2nm	160 Bh hP2nm	161 Hs hP2nm	162 65 Ts cl2nm	163 229 Og cF4nm	164 194 Tennessine hP2nm	165 194 Livermorium hP2nm	166 194 Tennessine hP2nm	167 194 Oganesson hP2nm	168 194 Tennessine hP2nm	169 194 Oganesson hP2nm	170 194 Tennessine hP2nm	171 194 Lu hP4nm
																		189 225 Ac cl2nm	190 225 Th cl2nm	191 139 Pa cl2nm	192 225 U cl2nm	193 62 Np cl2nm	194 11 Pu cl2nm	195 194 Am cl2nm	196 194 Cm cl2nm	197 194 Bk cl2nm	198 194 Cf cl2nm	199 Es cl2nm	200 Fm cl2nm	201 Md cl2nm	202 No cl2nm	203 Lr cl2nm		
Z Symbol Crys. Syst.		not used																																

FIG. 1. Periodic table of elements with the 71 elemental solids^{12,13} marked in green. Elements in white boxes are not contained in the set. The green boxes list stoichiometric formula, space group and metal(nm) or non-metal (nm).

Here, c denotes the speed of light and ν denotes the full potential $\nu = \nu_{\text{ext}} + \nu_{\text{H}} + \nu_{\text{XC}}$. To enforce gauge invariance against shifts of the potential zero, the eigenvalues are re-scaled

$$\epsilon_l^{\text{scaled}} = \frac{\epsilon_l^{\text{atomic}}}{1 + \langle \psi_l | \mathbf{p} \frac{c^2}{(2c^2 - v)^2} | \mathbf{p} | \psi_l \rangle} \quad (21)$$

in the ‘scaled ZORA’ treatment after self-consistency is reached. Alternatively, gauge invariance can be achieved in the ‘atomic ZORA’ treatment by not using the full potential v , but only the on-site free-atom potential in Equation (20).

3. GPAW

GPAW uses the projector augmented wave (PAW) method which includes both pseudo (PS) potential methods and the linear augmented-plane-wave (LAPW) method as well defined approximations¹⁴. The PAW method exploits that wave functions are vastly different in the bonding region between the nucleus where it is relatively smooth compared to the region near the nucleus where it can vary rapidly. The PAW method uses a linear transformation, $\hat{\tau}$, that maps the soft PS wave functions $|\tilde{\psi}_n\rangle$ to the all electron wave functions

Periodic Table of Chemical Elements for Binary solids

1 IA	2	18 VIIIA
1 225 H LiH ¹⁵	2 216 He	
3 225 Li LiF ¹⁶	4 216 Be BeS ²¹	5 194 B BN ⁵⁸
6 225 Na NaCl ¹⁷	7 225 Mg MgO ²²	8 225 C TiC ⁶¹
9 225 K KCl ¹⁸	10 225 Ca CaO ²³	11 225 N VN ³⁴
11 225 Rb RbCl ¹⁹	12 225 Sr SrO ²⁴	12 225 O CdO ⁵⁴
13 225 Cs CsCl ²⁰	14 225 Ba BaO ²⁵	13 216 Al AlP ⁵⁷
15 225 Fr RaF ²⁶	16 225 La-Lu Lanthanide Ac-Lr Actinide	14 216 Si SiC ⁶²
		15 216 P InP ⁵⁹
		16 216 S ZnS ⁶⁹
		17 216 Cl CuCl ⁷³
		18 216 Ar
		19 216 K KBr ⁷⁴
		20 216 Kr
		21 216 Xe
		22 216 Rn
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Formula	Number of atoms	Spacegroup (Symbol)	Formula	Number of atoms	Spacegroup (Symbol)
AlGaO ₃	5	221 (Pm $\bar{3}$ m)	Li ₂ SnCl	4	216 (F $\bar{4}$ 3m)
Ca ₂ CdP	4	216 (F $\bar{4}$ 3m)	MgGeN ₂	16	33 (Pna2 ₁)
Fe ₂ NiCu	4	225 (Fm $\bar{3}$ m)	Na ₂ IrZn	4	225 (Fm $\bar{3}$ m)
K ₂ LiBa	4	216 (F $\bar{4}$ 3m)	RuCO ₃	5	221 (Pm $\bar{3}$ m)
KAgO ₃	5	221 (Pm $\bar{3}$ m)	V ₂ CoB	4	216 (F $\bar{4}$ 3m)

TABLE V. List of ternary materials used to validate the model discussed in the main text for estimating numerical errors.

II. SUPPLEMENTARY DISCUSSION

A. Investigated Systems

With respect to materials, only the most simple and fundamental structures were considered in this study for the sake of simplicity and easy reproducibility. This includes the 71 elemental materials that have been studied in the aforementioned work by Lejaeghere et. al.¹³ (see Fig. 1) and an additional set of 82 representative binary materials (one for each element with charge ≤ 90 ; noble gases were not included). These structures were chosen from the Springer Materials Database by searching for each particular element for the energetically most stable binary structure known in the database. If more than one structure was reported in the database, the most stable (abundant) system with the simplest crystal structure (preferably cubic) was chosen. If a structure would qualify as representative for both components of the binary system, e.g., rock salt NaCl for both sodium and chlorine, the second most stable and simple structure was chosen as well, i.e., NaCl for Na and CuCl for chlorine. The starting lattice parameters are taken from experiment or previous calculations, and the materials are listed in Fig. 2 including space group, lattice parameter,s and reference to the original scientific publication. Likewise, a list of the ternary materials used in the study is given in Tab. V.

B. Investigated Properties

To lay a foundation for the investigation of numerical errors in DFT implementations, we decided to restrict ourselves to the most fundamental properties and systems so that the proposed calculations can be extended to all kinds of electronic-structure theory code.

With respect to properties, this includes: (i) Absolute total energies E_{tot} : The total energy as defined in Equation (7) is probably the most fundamental property calculated by any electronic-structure code. Note that it is variational with respect to the electron density $n(\mathbf{r})$ and only depends on the occupied electronic KS states. Given that it includes both the energetic contribution from core and valence electrons, converged numerical settings for both regions are necessary to achieve convergence in E_{tot} . (ii) Relative energy differences E_{rel} : If only energy differences E_{rel} are of interest, achieving full convergence in total energies E_{tot} is typically not necessary in DFT calculations due to benign error cancellation, especially in the core and semi-core region. To quantify this effect, we have computed the total energy difference E_{rel} between the original unit cell and an expanded cell with 5% larger volume and accordingly scaled internal atomic positions. Neither lattice vectors nor internal degrees of freedom were relaxed. E_{rel} can be regarded a good metric to quantify the numeric precision for energy differences, as appearing in potential-energy surfaces, elastic constants, and vibrational properties.

Let us note that the observed numerical errors are highly species-dependent (and PAW-potential-dependent in the case of GPAW) and do not follow any simple rule-of-thumb. This is exemplified in Fig. 3, which shows the numerical errors in total energies observed for FHI-aims and GPAW for two different basis sets. As evident from this data, the numerical errors thus mainly depend on the complexity of the chemical bonding and the ability of the chosen basis set to represent it. For this reason, the NAOs of FHI-aims perform better for rare gases as well as first- and second-row elements, which form covalent bonds, whereas the plane waves used in GPAW perform the better the softer the pseudopotentials, e.g., for delocalized, free-electron-like bonding featuring only valence electrons as observed in elemental aluminum. In the general case, in which all different form of bondings contribute, no trend can be identified. Note that for exciting the numerical errors are more evenly distributed, since the chosen, species-dependent precision metric ensures that all species exhibit comparable errors at the same settings.

C. LDA/PBE Comparison

As exemplified in Fig. 4a for the total energies, the numerical errors observed as a function of the basis set size are virtually identical at the LDA and PBE level. Similarly, numerical

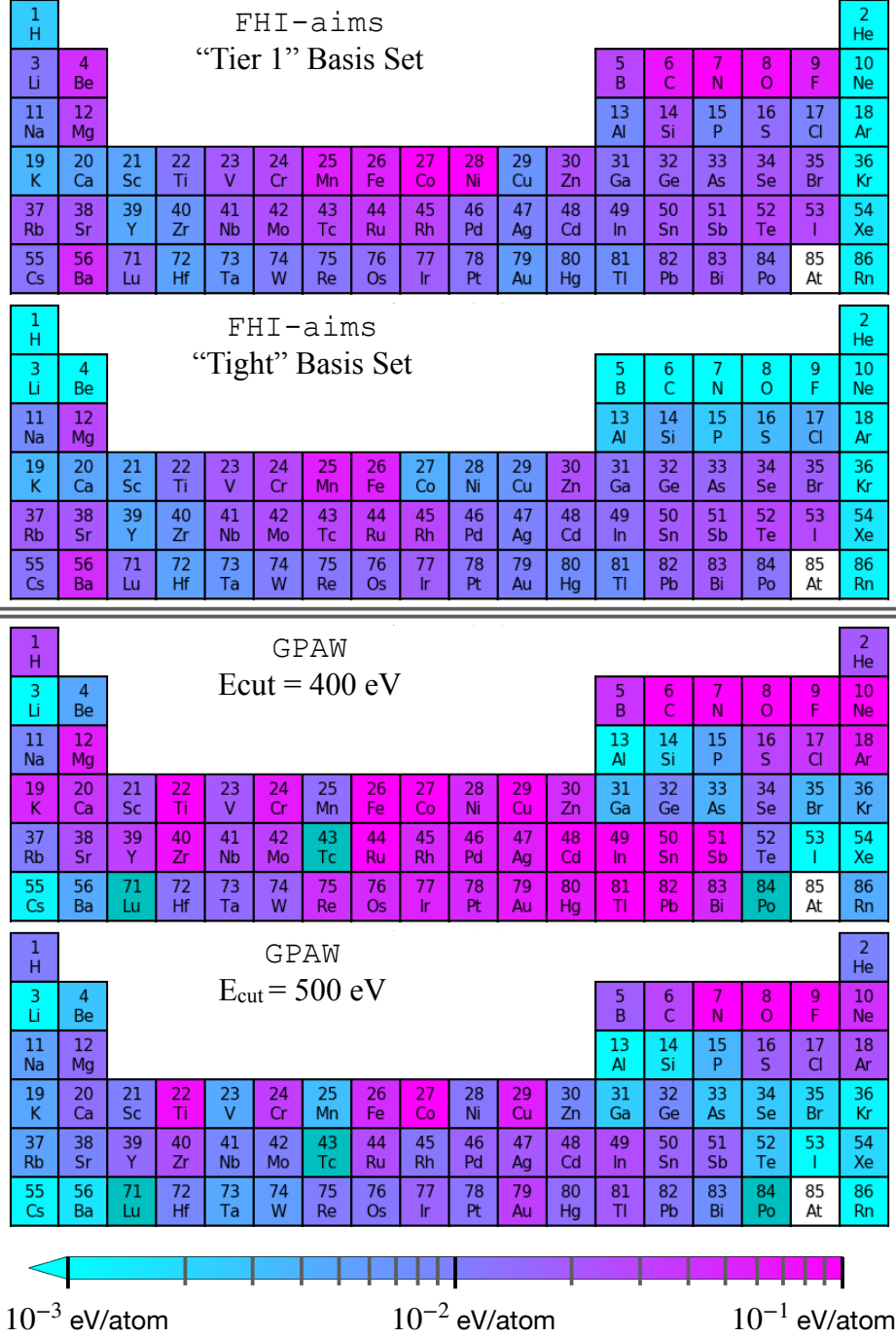


FIG. 3. (a) Total energy errors observed for the elemental solids (PBE, $8\text{\AA}$ $\mathbf{k}$ -point density) with FHI-aims (upper panel) and GPAW (lower panel) for ‘Tier 1’/‘Tight’ and $E_{\text{cut}} = 400/500$ eV basis sets, respectively.

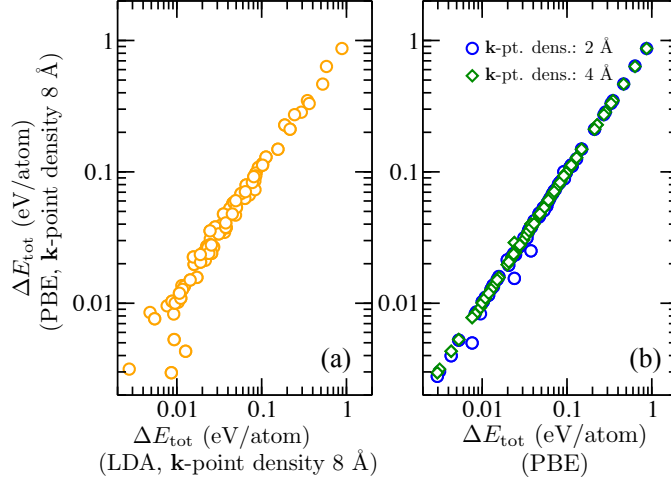


FIG. 4. (a) Errors observed at the LDA and PBE level in FHI-aims for the calculation of the elemental solids (for different basis sets). (b) Errors observed with different $\mathbf{k}$ -point densities in FHI-aims for the calculation of the elemental solids (for different basis sets). Note that in this case the error was determined by using consistent $\mathbf{k}$ -point densities, e.g., for the set with a $\mathbf{k}$ -point density of 2 Å calculations that are fully converged with respect to the basis set but use a $\mathbf{k}$ -point density of 2 Å were used as ‘fully converged’ reference.

errors stemming from the basis set and from the $\mathbf{k}$ -point density are independent from each other, as shown in Fig. 4b.

III. SUPPLEMENTARY REFERENCES

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- ¹ W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
 - ² D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
 - ³ J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
 - ⁴ J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - ⁵ A. Gulans, *et al.*, *J. Phys. Condens. Matter* **26**, 363202 (2014).
 - ⁶ V. Blum, *et al.*, *Comput. Phys. Commun.* **180**, 2175 (2009).
 - ⁷ E. Schrödinger, *Phys. Rev.* **28**, 1049 (1926).
 - ⁸ B. Delley, *J. Chem. Phys.* **92**, 508 (1990).

- ⁹ J. Baker, J. Andzelm, and A. Scheiner, *J. Chem. Phys.* **101**, 8894 (1994).
- ¹⁰ R. Stratmann, G. Scuseria, and M. Frisch, *Chem. Phys. Lett.* **257**, 213 (1996).
- ¹¹ A. Becke, *J. Chem. Phys.* **88**, 1053 (1988).
- ¹² K. Lejaeghere, V. V. Speybroeck, G. V. Oost, and S. Cottenier, *Crit. Rev. Solid State Mater. Sci.* **39**, 1 (2014).
- ¹³ K. Lejaeghere, *et al.*, *Science* **351**, aad3000 (2016).
- ¹⁴ P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ¹⁵ W. B. Zimmerman, *Phys. Rev. B* **5**, 4704 (1972).
- ¹⁶ P. Cortona, *Phys. Rev. B* **46**, 2008 (1992).
- ¹⁷ D. R. McCann, L. Cartz, R. E. Schmunk, and Y. D. Harker, *J. Appl. Phys.* **43**, 1432 (1972).
- ¹⁸ W. T. Barrett and W. E. Wallace, *J. Am. Chem. Soc.* **76**, 366 (1954).
- ¹⁹ V. T. Deshpande and D. B. Sirdeshmukh, *Acta Crystallogr.* **14**, 353 (1961).
- ²⁰ Z. Barnea and B. Post, *Acta Crystallogr.* **21**, 181 (1966).
- ²¹ H. Baaziz, Z. Charifi, F. El Haj Hassan, S. J. Hashemifar, and H. Akbarzadeh, *Phys. Status Solidi (b)* **243**, 1296 (2006).
- ²² C. Fang and G. de With, *Philos. Mag. A* **82**, 2885 (2002).
- ²³ A. Bolaran, F. Sanchez, S. Palomares, J. Aguilar, and G. Torres-Villaseaor, *J. Alloys Compd.* **436**, 335 (2007).
- ²⁴ Y.-D. Guo, X.-L. Cheng, L.-P. Zhou, Z.-J. Liu, and X.-D. Yang, *Phys. B: Condens. Matter* **373**, 334 (2006).
- ²⁵ T. Lv, D. Chen, and M. Huang, *J. Appl. Phys.* **100**, 086103 (2006).
- ²⁶ G. Schulze, *Z. Phys. Chem. B* **32**, 430 (1936).
- ²⁷ F. Hulliger and G. Hull Jr., *Solid State Commun.* **8**, 1379 (1970).
- ²⁸ H. Holleck and E. Smailos, *J. Nucl. Mater.* **91**, 237 (1980).
- ²⁹ G. Neumann, R. Kieffer, and P. Ettmayer, *Monatsh. Chem.* **103**, 1130 (1972).
- ³⁰ L. Brownlee, *J. Inst. Met.* **87**, 58 (1958).
- ³¹ V. Valvoda, *Phys. Status Solidi (a)* **83**, K123 (1984).
- ³² J. Gatterer, G. Dufek, P. Ettmayer, and R. Kieffer, *Monatsh. Chem.* **106**, 1137 (1975).
- ³³ K. Nakamura and M. Yashima, *Mater. Sci. Eng. B* **148**, 69 (2008).
- ³⁴ N. Pessall, R. Gold, and H. Johansen, *J. Phys. Chem. Solids* **29**, 19 (1968).
- ³⁵ J. D. Browne, P. R. Liddell, R. Street, and T. Mills, *Phys. Status Solidi (a)* **1**, 715 (1970).

- ³⁶ N. Schonberg, *Acta Metallurgica* **2**, 427 (1954).
- ³⁷ K. Page, *et al.*, *Solid State Sci.* **10**, 1499 (2008).
- ³⁸ C.-H. Leung and L. H. Van Vlack, *J. Am. Ceram. Soc.* **62**, 613 (1979).
- ³⁹ E. E. Rodriguez, *et al.*, *J. Am. Chem. Soc.* **129**, 10244 (2007).
- ⁴⁰ E. E. Rodriguez, *et al.*, *J. Appl. Phys.* **105**, 114901 (2009) .
- ⁴¹ T. Katsura, B. Iwasaki, S. Kimura, and S. Akimoto, *J. Chem. Phys.* **47**, 4559 (1967).
- ⁴² S. Butler and J. Gillson, *MRS Bull.* **6**, 81 (1971).
- ⁴³ B. P. Fokwa, P. R. Misse, M. Gillen, and R. Dronskowski, *J. Alloys Compd.* **489**, 339 (2010).
- ⁴⁴ N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950).
- ⁴⁵ O. Muller and R. Roy, *J. Less-common Met.* **16**, 129 (1968).
- ⁴⁶ A. A. Bolzan, C. Fong, B. J. Kennedy, and C. J. Howard, *Acta Crystallogr. B* **53**, 373 (1997).
- ⁴⁷ C. A. Barrett and E. B. Evans, *J. Am. Ceram. Soc.* **47**, 533 (1964).
- ⁴⁸ J. Waser, H. A. Levy, and S. W. Peterson, *Acta Crystallogr.* **6**, 661 (1953).
- ⁴⁹ W. J. Moore Jr. and L. Pauling, *J. Am. Chem. Soc.* **63**, 1392 (1941).
- ⁵⁰ R. W. G. Wyckoff and E. Posnjak, *J. Am. Chem. Soc.* **44**, 30 (1922).
- ⁵¹ V. Artjushenko, *et al.*, *Inorg. Mater.* **41**, 73 (2005).
- ⁵² H. Hirsch, A. de Cugnac, M. Gadet, and J. Pouradie, *C. R. Acad. Sci. B* **263**, 1328 (1966).
- ⁵³ X. Sun, *et al.*, *Solid State Commun.* **140**, 219 (2006).
- ⁵⁴ A. Cimino and M. Marezio, *J. Phys. Chem. Solids* **17**, 57 (1960).
- ⁵⁵ F. Ebert and H. Woitinek, *Z. Anorg. Allg. Chem.* **210**, 269 (1933).
- ⁵⁶ P. Deus, U. Volland, and H. A. Schneider, *Phys. Status Solidi (a)* **80**, K29 (1983).
- ⁵⁷ V. Geist and C. Ascheron, *Cryst. Res. Technol.* **19**, 1231 (1984).
- ⁵⁸ Q. Hu, *et al.*, and Y. Tian, *Phys. Rev. B* **73**, 214116 (2006).
- ⁵⁹ A. Antyukhov, *Inorg. Mater.* **22**, 426 (1986).
- ⁶⁰ T. Müürsepp and A. Haav, *Phys. Status Solidi (a)* **21**, K81 (1974).
- ⁶¹ J. Pflüger, J. Fink, W. Weber, K. P. Bohnen, and G. Crecelius, *Phys. Rev. B* **30**, 1155 (1984).
- ⁶² R. Iwanowski, K. Fronc, W. Paszkowicz, and M. Heinonen, *J. Alloys Compd.* **286**, 143 (1999).
- ⁶³ J. Stoemenos, S. Kokkou, and N. A. Economou, *Phys. Status Solidi (a)* **13**, 265 (1972).
- ⁶⁴ T. Chattopadhyay, J. Pannetier, and H. V. Schnering, *J. Phys. Chem. Solids* **47**, 879 (1986).
- ⁶⁵ V. Leute, A. Behr, C. Hanting, and H. Schmidtke, *Solid State Ion.* **68**, 287 (1994).

- ⁶⁶ E. F. Hockings, I. Kudman, T. E. Seidel, C. M. Schmelz, and E. F. Steigmeier, *J. Appl. Phys.* **37**, 2879 (1966).
- ⁶⁷ J. Woolley and D. Lees, *J. Less-common Met.* **1**, 192 (1959).
- ⁶⁸ F. Hund and R. Fricke, *Z. Anorg. Allg. Chem.* **258**, 198 (1949).
- ⁶⁹ X.-R. Chen, X.-F. Li, L.-C. Cai, and J. Zhu, *Solid State Commun.* **139**, 246 (2006).
- ⁷⁰ S. Deore, F. Xu, and A. Navrotsky, *Am. Mineral.* **93**, 779 (2008).
- ⁷¹ J. Baudour, M. Granger, L. Toupet, R. Granger, and R. Triboulet, *J. Phys. Chem. Solids* **50**, 309 (1989).
- ⁷² V. Kanchana, G. Vaitheeswaran, A. Svane, and A. Delin, *J. Phys. Condens. Matter* **18**, 9615 (2006).
- ⁷³ B. R. Lawn, *Acta Crystallogr.* **17**, 1341 (1964).
- ⁷⁴ N. M. Butt, K. D. Rouse, M. W. Thomas, and B. T. M. Willis, *Acta Crystallogr. A* **34**, 840 (1978).
- ⁷⁵ R. Davis and C. H. Kennard, *J. Solid State Chem.* **64**, 217 (1986).
- ⁷⁶ B. Morosin, *J. Chem. Phys.* **49**, 3007 (1968).
- ⁷⁷ P. Ettmayer, J. Waldhart, A. Vendl, and G. Banik, *Monatsh. Chem.* **111**, 1185 (1980).
- ⁷⁸ P. Schobinger-Papamantellos, P. Fischer, O. Vogt, and E. Kaldis, *J. Phys. Condens. Matter* **6**, 725 (1973).
- ⁷⁹ T. D. Chikalla, C. E. McNeilly, and F. P. Roberts, *J. Am. Ceram. Soc.* **55**, 428 (1972).
- ⁸⁰ R. J. Gambino, R. R. Ruf, T. R. McGuire, and P. Fumagalli, *J. Appl. Phys.* **70**, 6386 (1991).
- ⁸¹ R. Brown and N. Clark, *J. Inorg. Nucl. Chem.* **36**, 2507 (1974).
- ⁸² H. R. Child, M. K. Wilkinson, J. W. Cable, W. C. Koehler, and E. O. Wollan, *Phys. Rev.* **131**, 922 (1963).
- ⁸³ D. Li, *et al.*, *J. Magn. Magn. Mater.* **140-144**, 1169 (1995).
- ⁸⁴ H. Klesnar and P. Rogl, *High Temp. High Press.* **22**, 453 (1990).
- ⁸⁵ W. H. Zachariasen, *Acta Crystallogr.* **1**, 265 (1948).
- ⁸⁶ R. Street and T. Waters, *J. Less-common Met.* **5**, 295 (1963).