

AB INITIO CALCULATION OF THE BCC FE-M (M=Ti, V, Nb, Mo) PHASE DIAGRAMS IN THE IRREGULAR TETRAHEDRON APPROXIMATION¹

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Abstracts

The metastable phase diagrams of the bcc-based ordering equilibria in the Fe-M (M = Ti, V, Nb, Mo) systems have been calculated by the cluster expansion method, through the combination of FP-LAPW and CVM. In spite of being neighbors in the periodic table, these four alloying elements result in radically different phase diagram topologies when alloyed with iron. This result contrasts with usual regularities (e.g. the Hume-Rothery rules) typically observed in other intermetallic compounds. The results are discussed considering the Density of States (DOS) functions of the B2 compounds in the four systems and correlating their Cohesive Energies with total magnetic moment.

Keywords: Full potential; Linear-augmented plane wave (FP-LAPW) method; Cluster Variation Method (CVM); Magnetic interactions; Order-disorder transformations.

CÁLCULO POR PRIMEIROS PRINCÍPIOS DOS DIAGRAMAS DE FASES DOS SISTEMAS FE-M (M = Ti, V, Nb, Mo) CCC NA APROXIMAÇÃO DO TETRAEDRO IRREGULAR

Resumo

Os diagramas de fases metaestáveis das relações de ordenação baseadas no reticulado CCC foram calculados para os sistemas Fe-M (M = Ti, V, Nb e Mo) pelo método da expansão em clusters, pela combinação do método FP-LAPW e do CVM. Apesar de serem vizinhos na tabela periódica, os quatro elementos de liga produzem topologias de diagramas de fases radicalmente diferentes quando ligados ao ferro. Este resultado contrasta com as regularidades (e.g. regras de Hume-Rothery) usualmente observadas para outros materiais intermetálicos. Os resultados são discutidos em conexão com as funções Densidade-de-estados (DOS) dos compostos B2 nos quatro sistemas, correlacionando suas energias de formação com o momento magnético total do composto.

Palavras-chave: Método Full-potential; Linear-augmented plane wave (FP-LAPW); Método Variacional de Clusters (CVM); Interações magnéticas; Reações ordem-desordem.

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INTRODUCTION

Intermetallic compounds have puzzled materials scientists since their discovery. These materials defy the usual rules of chemical stoichiometry based on the concept of chemical valence for acid/base equilibria. Nonetheless they indeed obey some periodic table-based regularities, which have led some researchers to develop “empirical” criteria, such as the Hume-Rothery rules, where the stability of a given structure is attributed to size-factors, electronegativity differences and to a certain electron/atom concentration range.⁽¹⁾ Size-effects, for example, have also been proposed to justify the effect of alloying elements upon the order-disorder temperature for the B2/D0₃ equilibrium in Fe-Al-X alloys.^(2,3) With the development of advanced ab initio techniques in recent years, a reliable check of these “phenomenological” rules against the calculated electron structure of the alloys became possible. As an example, Lee and Hoistad recently showed that a simple quantum mechanical model is able to account for the structure of elements between groups 6 and 17 of the periodic table.⁽⁴⁾ Some periodic table correlations are also experimentally observed for order/disorder equilibria in body centered cubic (BCC) alloys. As an example, systems Fe-X (X = Al, Si, Ga, Ge) all present order/disorder transitions in the BCC field at the iron-rich side of the phase diagrams,⁽⁵⁾ which can be reproduced by the Ising model with nearest and next-nearest attractive interactions between unlike atoms.⁽⁶⁾

The aim of the present work is to verify whether a similar correlation can be found in BCC alloys of iron with an early transition metal, in the present case Fe-M (M = Ti, V, Nb, Mo). It turns out that these systems present radically different BCC ordering equilibria. This unexpected result is then analyzed by considering the Density-of-States (DOS) functions for the ordered compounds B2-FeM and D0₃-Fe₃M and by correlations between their formation energies and the permanent magnetic moment.

METHODOLOGY

The present calculations follow the Cluster Expansion Method (CEM) of alloy phase diagram calculation.⁽⁷⁾ In the CEM the formation energies at the ground state of a set of stoichiometric ordered compounds (which are related to a common disordered lattice) are calculated by solving one particle Schrödinger’s equation using an electronic structure calculation tool. This set forms a basis for the truncated expansion of the internal energy of the system at all temperatures and compositions, which are then used as input in a statistical mechanics method to calculate the phase diagram. The set used in the present work corresponds to the A2 (Fe, Ti, V, Nb, Mo), B2 (FeTi, FeV, FeNb, FeMo), D0₃ (Fe₃Ti, Fe₃V, Fe₃Nb, Fe₃Mo, FeTi₃, FeV₃, FeNb₃, FeMo₃) and B32 (FeTi, FeV, FeNb, FeMo) compounds, which allows the thermodynamic description of the respective binary systems in terms of the irregular tetrahedron approximation of the Cluster Variation Method (CVM).^(8,9)

We used the Full-potential, linear-augmented plane wave (FP-LAPW) method, as embodied in the WIEN03 code, for the calculation of the total energies of the compounds.⁽¹⁰⁾ The FP-LAPW method allows very precise computation of total energies and charge densities and is, at the moment, one of the most accurate methods for electronic structure calculation in solids. The exchange-correlation part of the functional has been approximated using the Generalized Gradient Approximation (GGA), in the Perdew-Burke-Ernzerhof implementation,⁽¹¹⁾ and all calculations have been performed in the spin-polarized mode since at least one of

the ground states (A2 Fe) is known *a priori* to be ferromagnetic. The equilibrium lattice constants of all structures have been optimized through the calculation of the minimum value of the total energy. Optimization of static relaxations is not necessary, since all calculated compounds are quite symmetric (i.e. there are no internal site position degrees-of-freedom in their crystallographic models). As the total energy is the important parameter in the present case, particular care was taken in performing the convergence tests. Following the WIEN03 notation the convergence of the order of 10^{-4} Ry (1 Ry = 13.6 eV) has been achieved by using suitable values of the RK_{max} , l_{max} and number of k -points, which are control parameters of the convergence in the FP-LAPW calculation (see the Appendix).

The calculated total energies of the compounds are used as input parameters in the statistical mechanics formalism to proceed with the calculation of the phase diagrams. In the present work the cluster variation method (CVM) in the irregular tetrahedron approximation has been adopted for this purpose. The procedure used in the CVM calculation has been thoroughly outlined in previous publications by the authors.^(6,8,9) The reader is referred to these publications for details. For the purposes of the present work it is sufficient to state that the complete thermodynamic description of a given binary system (say Fe-M) requires setting four cluster interaction parameters: $w_{FeM}^{(1)}$, $w_{FeM}^{(2)}$, \tilde{w}_{FeMFeM} and $\tilde{w}_{MFeFeFe}$, the first two corresponding respectively to nearest and next-nearest neighbor interactions and the remaining to excess tetrahedron interactions.⁽¹²⁾ These parameters are obtained from the compound formation energies by the procedure described in Gonzales-Ormeño, Petrilli e Schön.⁽⁶⁾

RESULTS

Table 1 shows the results for total energies E_{tot} (in Ry = 13.6 eV), equilibrium lattice parameter a_0 (in nm) and total magnetic moment (in Bohr magnetons, μ_B) for all compounds investigated in the present work. The table also shows the FP-LAPW parameters corresponding to these converged values. Table 2 shows the corresponding formation energies in the reference state of the mechanical mixture of the pure BCC components ($\Delta^f U_{Fe_xM_y}^\Phi$), using the procedure described in Gonzales-Ormeño, Petrilli e Schön.⁽⁹⁾ This table also shows the values of the CVM cluster interactions, CIs.⁽⁸⁾ Figure 1 shows the CVM –calculated phase diagrams of the four systems.

Table 1. Total energies E_{tot} (in Ry = 13.6 eV) per unit formula, equilibrium lattice parameter a_0 (in nm) and total magnetic moment (in Bohr magnetons, μ_B) for the investigated compounds. The FP-LAPW parameters⁽⁸⁾ corresponding to these converged values are also shown at the Table.

Compound	Structure	Atoms in unit formula	RK_{max}	l_{max}	# k -points	E_{tot}	a_0	μ
Fe	A2	1	10	11	560	-2527.2644	0.285	2.23
Ti	A2	1	10	11	560	-1698.6495	0.326	0
V	A2	1	10	11	560	-1887.7812	0.300	0
Nb	A2	1	10	11	406	-7510.7806	0.332	0
Mo	A2	1	11	12	406	-7954.6892	0.317	0
FeTi	B2	2	10	10	286	-4225.9811	0.297	0
FeV	B2	2	10	10	286	-4415.0618	0.290	0.83
FeNb	B2	2	10	10	286	-10038.0461	0.308	1.02
FeMo	B2	2	11	11	286	-10481.9285	0.303	2.06
Fe ₃ Ti	D0 ₃	4	10	10	286	-9280.5064	0.585	5.18
Fe ₃ V	D0 ₃	4	10	10	286	-9469.6097	0.575	4.87
Fe ₃ Nb	D0 ₃	4	10	10	286	-15092.5852	0.593	5.16
Fe ₃ Mo	D0 ₃	4	10	11	286	-15536.4493	0.589	6.28
FeTi ₃	D0 ₃	4	10	10	286	-7623.2453	0.620	0
FeV ₃	D0 ₃	4	10	10	286	-8190.6472	0.585	0
FeNb ₃	D0 ₃	4	10	10	286	-25059.5993	0.638	0
FeMo ₃	D0 ₃	4	10	11	165	-26391.2868	0.622	2.07
Fe ₂ Ti ₂	B32	4	10	10	286	-8451.8808	0.602	2.19
Fe ₂ V ₂	B32	4	10	10	286	-8830.1228	0.581	2.15
Fe ₂ Nb ₂	B32	4	10	10	286	-20076.0650	0.615	2.34
Fe ₂ Mo ₂	B32	4	10	11	165	-20963.8003	0.606	2.04

DISCUSSION

Analysis of Figure 1 shows that the four systems here investigated present radically different phase diagram topologies in the metastable BCC equilibria. This unexpected result contrasts with the above mentioned periodic-table regularities, observed in the case of other intermetallics cases. For example, Fe-Ti shows a quite stable B2 phase and a two-phase field at the titanium-rich side, corresponding to the first-order equilibria between this compound and the A2-Ti phase. This is consistent

with the experimental phase diagram.⁽⁵⁾ Fe-V, on the other hand, show no sign of a stable B2 compound, but present two stable D0₃ compounds, with a quite unusual extended solubility between Fe₃V and FeV₃. No indication of these compounds is found in the experimental phase diagrams due the existence of a more stable phase (5). Fe-Nb presents a very unusual phase diagram topology: the system presents ordering character at the iron-rich side and a phase separating character at the niobium-rich side, but the formation energies of the compounds are quite low (which correspond also to a low temperature scale in the phase diagram), and this means that the system should not deviate significantly from the ideal thermodynamic behavior at high temperatures. Notice also the appearance of a B2 phase at high temperature and quite outside its ideal stoichiometry. As in the case of Fe-V, the direct confirmation of these topological relations in the experimental phase diagram is prevented by the existence of more stable intermetallics.⁽⁵⁾ Finally, Fe-Mo shows a typical phase separating behavior, consistent with the present thermodynamic description of the bcc phase in CALPHAD-type assessments.⁽¹³⁾

Figure 2 shows the DOS functions of the four B2 compounds. As already observed (Table 1), in the transition from FeTi to FeMo one observes the onset of ferromagnetism in the compounds. As a consequence the DOS changes, first by an almost rigid displacement of the spin-down states towards higher energies (from FeTi to FeV) then by shape changes in FeNb and FeMo, which only barely resemble the one of the non-magnetic compound (FeTi). As a consequence progressively less d states become available for the electrons below the Fermi level (E_F). This is probably related with the decrease in stability of the B2 compound and implies that the key factor in explaining the lack of correlation in the phase diagram topologies is related to ferromagnetism.

Figure 3 shows relative stabilities of the B2 compounds (against separation into the two disordered components) and D0₃-Fe₃M compounds (against separation into A2-Fe and the B2-FeM compound) as a function of the total magnetic moment of the alloy. One observes, that, indeed, there is a correlation between the magnetic moment and the stabilities of the compounds. The analysis of this figure, however, clearly shows that the effect of the magnetic moment is different for both classes of compounds (being stronger for the B2 compounds). Therefore one could speculate that two effects act in the alloys of iron with the early transition metals:

1. onset of ferromagnetism leads to complex changes in the DOS functions of the compounds forming the basis for the CEM expansion, which depend not only on the iron content of the alloy, but also on structural effects.⁽¹⁴⁾
2. these changes affect the formation energies of the different compounds in different manner, leading to the observed changes in topology of the phase diagrams.

Table 2. Formation energies (in kJ/mol), CVM cluster interactions and CI (in $k_B K$), for the stoichiometric compounds of Table 1.

Compound	Structure	$\Delta^f U_{Fe_x M_y}^\Phi$	CI
FeTi	B2	-44.07	$w_{FeTi}^{(1)} = -1325.1$
FeTi ₃	D0 ₃	-10.52	$w_{FeTi}^{(2)} = +923.3$
FeTi	B32	-17.34	$\tilde{w}_{FeTiFeTi} = -327.5$
Fe ₃ Ti	D0 ₃	-20.91	$\tilde{w}_{TiFeFeFe} = -208.3$
FeV	B2	-10.634	$w_{FeV}^{(1)} = -319.7$
FeV ₃	D0 ₃	-12,866	$w_{FeV}^{(2)} = -605.6$
FeV	B32	-10.371	$\tilde{w}_{FeVFeV} = +201.3$
Fe ₃ V	D0 ₃	-11.684	$\tilde{w}_{VFeFeFe} = +23.7$
FeNb	B2	-0.787	$w_{FeNb}^{(1)} = -23.7$
FeNb ₃	D0 ₃	+2.363	$w_{FeNb}^{(2)} = +221.1$
FeNb	B32	+8.271	$\tilde{w}_{FeNbFeNb} = +63.2$
Fe ₃ Nb	D0 ₃	-3.807	$\tilde{w}_{NbFeFeFe} = -123.6$
FeMo	B2	+16.226	$w_{FeMo}^{(1)} = +487.9$
FeMo ₃	D0 ₃	+14.697	$w_{FeMo}^{(2)} = +527.9$
FeMo	B32	+18.445	$\tilde{w}_{FeMoFeMo} = -83.1$
Fe ₃ Mo	D0 ₃	+14.697	$\tilde{w}_{MoFeFeFe} = -56.8$

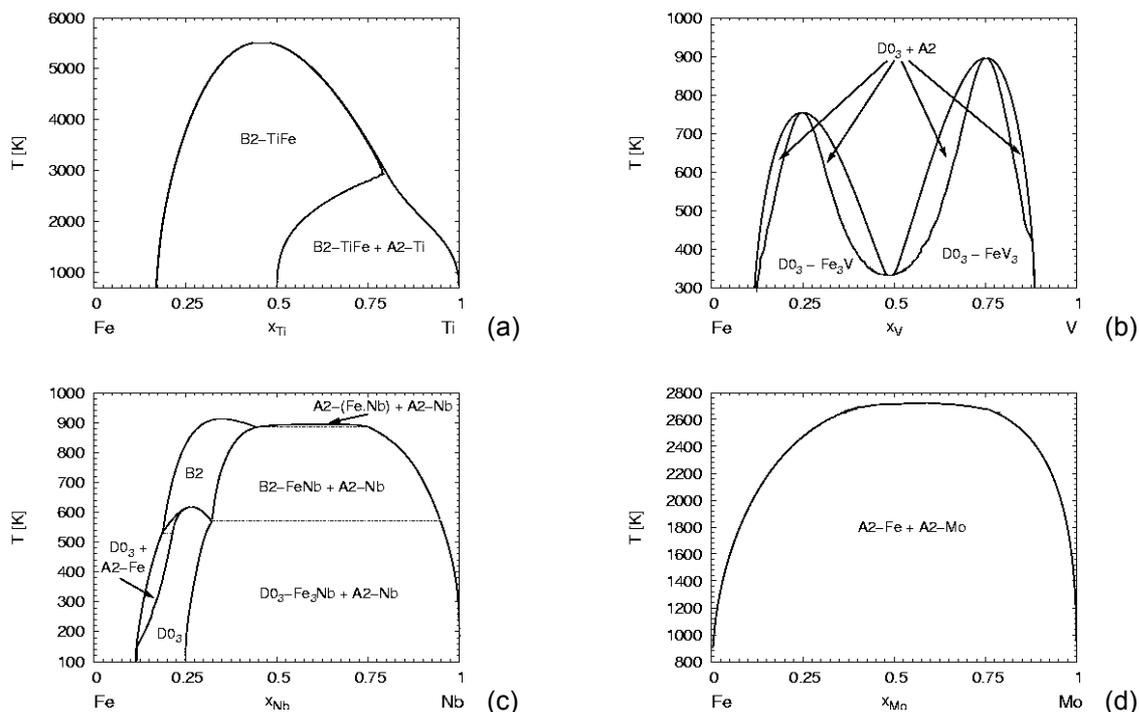


Figure 1. CVM-calculated phase diagrams using the parameters of Table 2: (a) – BCC Fe-Ti, (b) – BCC Fe-V, (c) BCC – Fe-Nb and (d) BCC – Fe-Mo.

CONCLUSIONS

The formation energies of 16 ordered compounds of binary iron systems with the early transition metals (Fe-M, where M = Ti, V, Nb and Mo) have been calculated using the FP-LAPW method. These formation energies have been used as input parameters for the CVM to calculate the phase diagrams of the metastable phase equilibria in the irregular tetrahedron approximation.

The four systems present radically different phase diagrams, ranging from a strong ordering system (Fe-Ti) to a strong phase separating system (Fe-Mo), with Fe-V and Fe-Nb representing intermediate complex cases. These different topologies arise fundamentally from the effect of magnetic ordering and, specially, in the interplay between the d electrons of Fe and M, as demonstrated by the changes in the DOS functions of the B2 compounds.

A correlation was observed between total magnetic moment and compound stability for the B2 and DO_3 - Fe_3M compounds. This correlation is such that the higher the magnetic moment, the lower is the stability of the compounds. The strength of this correlation, however, is different for both compounds, which leads to the different phase diagram topologies.

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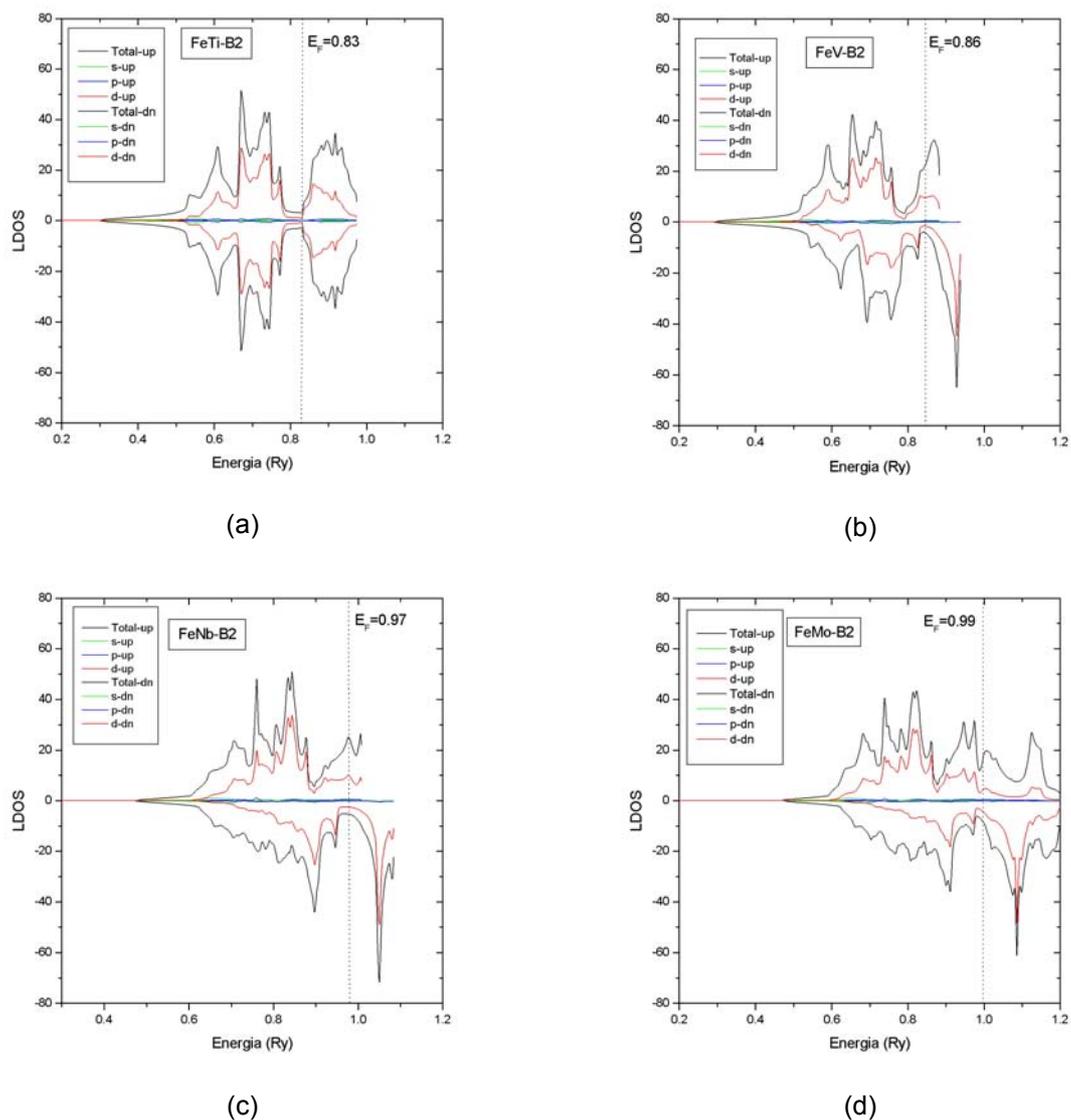


Figure 2. Electron DOS functions of the four B2 compounds, as calculated by the FP-LAPW method in the WIEN03 implementation.

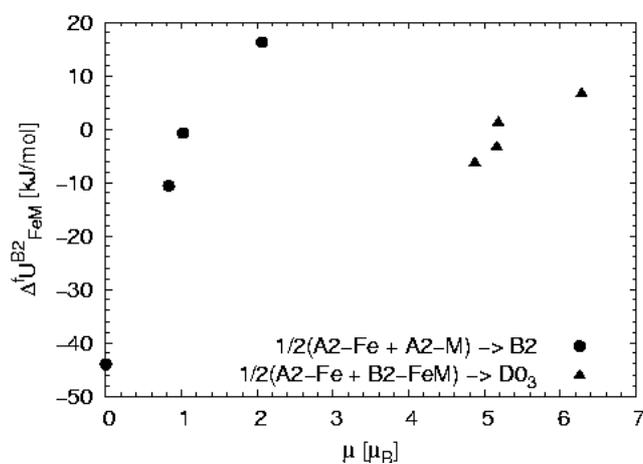


Figure 3. Variation of the compound stabilities of the B2 (against separation into A2-Fe and A2-M) and D0₃-Fe₃M (against separation into A2-Fe and B2-FeM) as a function of the total magnetic moment.

APPENDIX – FP-LAPW

The key issue in modeling the electron structure of transition metals is the role of the inner d band in bonding. These electron states are located close to the core of the atom and, therefore, show a much more localized character, similar to the atomic states. They are, however, able to perform hopping between neighboring atoms, contributing to the metallic bond. The rapid variation of the itinerant electron wave function near the core of the atom (characteristic of the atomic-like functions) is the main difficulty associated with the calculation of by reciprocal space methods (using Bloch's theorem).⁽¹⁵⁾ Standard methods for electron structure calculation⁴ in the reciprocal space (or k-space, as it is usually known) rely in the division of the system into core states and an interstitial region between the atoms and the use of different bases to describe the electron wave function in each region.⁽¹⁵⁾ In the FP-LAPW method, for example, the space is divided into spheres centered at the atoms and atomic-like functions (up to a maximum value of the angular momentum quantum number, l_{max}) are used as basis, and the interstitial region is described using plane-waves.⁽⁶⁾ The wave functions are then matched by value and slope at the interface between spheres. This shows that a FP-LAPW calculation is sensitive to the choice of the radius for the spheres. A control parameter for this sensibility is called RK_{max} , by definition the product of the lowest sphere radius R by the largest lattice vector \mathbf{G} included in the plane wave expansion: $RK_{max} = \min\{R\} \max\{|\mathbf{G}|\}$.⁽⁶⁾ Finally, Schrödinger's equation must be solved numerically in the k-space and the number of points in the corresponding mesh introduces a third control parameter in FP-LAPW calculation (# k -points).⁽⁶⁾ The precision of the solution increases with an increase of either l_{max} , RK_{max} or # k -points, but the computational cost increases as well, therefore the optimal values for each parameter depends on the compound.⁽⁸⁾

⁴ As the Linear Muffin-Tin Orbital, LMTO, or the even the LAPW method.

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