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Vacancy formation energies in fcc metals: Influence of exchange-correlation functionals and correction schemes

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The performance of various exchange-correlation functionals (LDA, PBE, PW91, and AM05) in predicting vacancy formation energies has been evaluated for 12 fcc metals. A careful analysis of the results shows that differences between the theoretical result and experiment are mainly related to the way the various exchange-correlation functionals describe the internal surface of the vacancy. Based on this insight we propose a modified version of the correction scheme of Mattsson, Wixom, and Armiento [Phys. Rev. B **77**, 155211 (2008)]. Applying this approach to our results yields a perfect alignment of vacancy formation energies for all exchange-correlation functionals. These corrected values are also in very good agreement with the vacancy formation energies obtained in experiment.

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I. INTRODUCTION

Vacancies are common point defects in all crystalline metallic systems. Although their concentration is small (typically 10^{-3}–10^{-4} in pure metals at the melting temperature)[1] they play an important role in transport and mechanical properties of metals. For example, self-diffusion in close-packed metals mainly occurs by vacancy related mechanisms. Also segregation of vacancies in the form of pores or even cracks may lead to a degradation of material resistance.[2]

The key quantity for vacancy related properties is its formation energy. In the dilute limit the concentration of vacancies at a given temperature is exponentially proportional to the vacancy formation energy, where a lower vacancy formation energy yields a higher concentration of thermodynamically stabilized vacancies.

Vacancy formation energies are usually determined indirectly by using their exponential relation to vacancy concentration. Commonly employed experimental techniques are differential dilatometry, resistivity, calorimetry and more established positron annihilation spectroscopy (PAS).[1] Most of these experiments can only be done at sufficiently high temperatures, which are needed to generate sufficiently high vacancy concentrations and equilibration.

An alternative approach is the determination of vacancy properties with *ab initio* calculations. Usually these calculations are done at 0 K and do not consider the effect of temperature on the vacancy formation energy. Only recently a full *ab initio* treatment of vibronic effects (including anharmonicity) and their impact on vacancy formation energies became tractable.[3]

Over the last decades several studies on vacancies at 0 K in different metals have been published. Korzhavyj *et al.*[4] studied vacancies in transition and noble metals using the order-N locally self-consistent Green's function method together with local-density approximation (LDA). Several studies[5–7] showed that LDA gives generally more accurate vacancy formation energies when comparing with various generalized gradient approximations (GGA), e.g., of Perdew, Burke, and Ernzerhof (PBE)[8,9] and of Perdew and Wang (PW91).[10] There are several reasons for this trend. First, LDA and GGA describe the binding of metals differently and therefore show already for bulk metals discrepancies in the parameters describing the equation of state. For magnetic materials they also predict different values for the magnetic moments.[11] These differences often modify other parameters (e.g., lattice constants), which subsequently affect also the vacancy formation energies. The process of forming a vacancy includes the creation of an internal free surface. LDA tends to describe internal surfaces better than GGA. The reason is a well-known cancellation effect:[12] LDA largely overestimates the exchange energy of a free metal surface, but underestimates by approximately the same magnitude the correlation energy. This results in a reasonable net total value of the surface energy.[12] GGA results vary depending on the parametrization of the exchange-correlation (xc) functional in use. For example, for PBE the exchange surface energy is underestimated but the correlation surface energy is only slightly overestimated, resulting in too small vacancy formation energies.[12]

To overcome the shortcomings of GGA and LDA in describing the vacancy internal surface, a postprocessing correction scheme has been proposed by Carling *et al.*[5] and successively applied to vacancy formation energies in Al,[5] Pt, Pd, and Mo.[6] The idea of this scheme is to add to the calculated vacancy formation energy the xc induced error of the surface energy. The error is estimated by considering a jellium surface[12] or a jellium sphere,[13] for which exact or nearly exact methods, such as, e.g., quantum Monte Carlo simulations can be applied.

In a subsequent study Armiento and Mattsson proposed a new xc functional, AM05,[14,15] to overcome the difficulties of available GGA functionals (PBE and PW91) in the description of point defects. The accuracy of the AM05 functional in describing the vacancy formation energies was tested and compared against other functionals for three fcc metals (Al, Cu, and Ni) by Delczeg *et al.*[7] Based on their results the authors concluded that LDA provides a better description of vacancy formation energies than PBE and AM05.

In this work we discuss possible reasons for the discrepancy between vacancy formation energies obtained by different xc functionals. To derive systematic trends we perform our calculations for a large set of 12 pure fcc metals and using

LDA, PBE, PW91, and AM05. Employing a modification of the correction scheme proposed in Ref. [16], we obtain consistent vacancy formation energies for all xc functionals. The corrected energies significantly improve agreement with experiment.

II. METHODOLOGY

Equilibrium geometry and formation energies have been computed employing density-functional theory[17,18] as implemented in the Vienna Ab Initio Simulation Package (VASP).[19–21] We use LDA,[22,23] two flavors of the GGA, PBE,[8,9] and PW91,[10] as well as the AM05,[14,15] which is based on the subsystem functional approach. Standard (scalar-relativistic) PAW potentials[24,25] as implemented in VASP have been used.

Careful convergence tests revealed that a mesh of 6912 k-point×atoms (corresponding to a $6 \times 6 \times 6$ Monkhorst-Pack mesh in a $2 \times 2 \times 2$ supercell) is sufficient to achieve an accuracy in the total energy of better than 2 meV/atom. For the Fermi-surface smearing the first-order Methfessel-Paxton method[26] is used. A smearing width of 0.1 eV is chosen and ensures that the corresponding error in the 0-K extrapolated energy is less than 1 meV/atom. In the equilibrium configuration the forces on each atom are below 0.01 eV/Å.

In order to determine the equilibrium lattice constant and bulk modulus we varied the lattice constant in the range of ±5% around the experimental one and used ten sample points. The obtained energy-volume dependency is fitted to a Birch-Murnaghan equation of state.[27] The fit provides the equilibrium lattice constant and bulk modulus. The cohesive energies of the ideal bulk structures are obtained with respect to the corresponding spin-polarised isolated atoms.

In order to estimate the impact of the artificial interaction of a point defect with its images due to the employed supercell approach, we analyzed the formation energy with respect to supercell size. The results of our analysis show that due to the dense packing in an fcc crystal already a $2 \times 2 \times 2$ supercell with 32 (31) host atoms is sufficient to achieve an accuracy in the vacancy formation energy of better than 0.1 eV for all considered metals.

The vacancy formation volume Ω_f and the vacancy formation energy E_f are obtained from constant pressure calculations and are equal to $X_\mathrm{f} = X_\mathrm{tot}^\mathrm{vac} - \frac{N-1}{N} X_\mathrm{tot}^\mathrm{bulk}$, where N is the number of lattice sites in the supercell and X is its total volume or total energy, respectively.

The description of the internal surface energy due to the approximate nature of the xc functionals can be improved by one of the correction schemes proposed previously.[5,6] Typically a correction term $\Delta\sigma \cdot A^\mathrm{int}$ is applied. Here $\Delta\sigma$ is the correction of the surface energy, which is given by the difference between an exact (or nearly exact) solution and the solution based on the specific xc functional. To compute the area of the internal surface of a vacancy (A^int) various strategies and assumptions have been proposed. In the original work of Carling *et al.*[5] the internal surface of a vacancy has been approximated by a sphere with the radius found from a juxtaposition of charge densities of a vacancy and of a jellium surface. In the work of Mattsson and Mattsson[6] the radius of the spherical internal surface of a vacancy was assumed to be proportional to the lattice constant of the system. To align their procedure the authors used the radius obtained by Carling *et al.*[5] for the Al vacancy and rescaled it by the ratio between the lattice parameter of the considered fcc metal and Al.

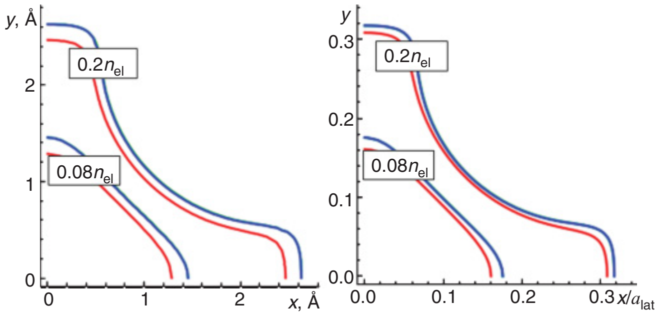

FIG. 1. (Color online) Charge density in the vicinity of a vacancy in Ag plotted for the (100) plane in Cartesian (left) and relative (right) coordinates. Isosurfaces (for the given fraction of the mean charge density) are indicated by red/light (LDA) and blue/dark (GGA, PBE, and PW91 are indistinguishable) lines.

Our analysis of the charge density in the vicinity of a vacancy shows that the internal surface of a vacancy can only very approximately be considered as a sphere (see Fig. 1). Furthermore, the shape of the charge density changes often dramatically from one metal to another making the scaling to the vacancy area in Al questionable. A more general approach, which requires no implicit knowledge about the surface area, has been proposed and applied to the Si interstitial formation energy recently.[16] In this approach the area of the internal surface is considered to be unknown, but equal for all xc functionals (LDA, PBE, and PW91). Furthermore, a fixed ratio of 0.29:0.76:1 has been applied for LDA:PBE:PW91 surface energy corrections. In the following we propose a modified version of this approach which releases some of the approximations involved in the previous schemes: First, we allow the area of the vacancy internal surface to be different for different xc functionals. Furthermore, no fixed ratio for surface energy corrections is applied in this work, so the intrinsic exchange-correlation surface energy correction can be found using the value of the bulk electronic density specific for each xc functional (n_el in Table I).

An interesting observation based on a detailed analysis of our results is that the charge densities in the vicinity of a vacancy are for the same element, but different xc functionals very similar, provided relative coordinates (i.e., normalized by the lattice parameter specific for each xc functional) are used (see Fig. 1). Therefore the shape and the size of the vacancy internal surface is also the same for all xc functionals in these coordinates. If the area of the vacancy internal surface is x in relative coordinates, in absolute coordinates it has to be scaled by the xc functional dependent square of the lattice constant $[(a^\mathrm{xc})^2]$. The corrected value for the vacancy formation energy is then

$$\tilde{E}_\mathrm{f}^\mathrm{xc} = E_\mathrm{f}^\mathrm{xc} + x(a^\mathrm{xc})^2 \Delta\sigma_\mathrm{cor}^\mathrm{xc}\left(n_\mathrm{el}^\mathrm{xc}\right), \tag{1}$$

where E_f^xc is the noncorrected vacancy formation energy from a DFT calculation with a certain xc functional (see Table II), and $\Delta\sigma_\mathrm{cor}^\mathrm{xc}(n_\mathrm{el}^\mathrm{xc})$ is the intrinsic, xc functional specific surface correction. The latter can for a specific electronic density ($n_\mathrm{el}^\mathrm{xc}$) directly be taken from Fig. 2 of Ref. 42.

TABLE I. Characteristics of bulk metals calculated with different xc functionals without zero-point and finite temperature corrections and experimental results. The average discrepancy from experiment based on the results of all metals is for each xc functional and for each characteristic parameter also shown.

		Ag	Al	Au	Ca	Cu	Ir	Ni	Pb	Pd	Pt	Rh	Th	Error (%)
a (Å)	LDA	4.027	3.982	4.072	5.305	3.534	3.824	3.438	4.886	3.862	3.914	3.772		−1.5
	PBE	4.169	4.048	4.180	5.526	3.640	3.880	3.526	5.034	3.958	3.981	3.845	5.044	0.9
	PW91	4.163	4.055	4.180	5.545	3.640	3.885	3.523	5.032	3.961	3.990	3.847	5.047	0.9
	AM05	4.058	4.013	4.082	5.494	3.570	3.830	3.457	4.942	3.871	3.909	3.767	4.943	−0.9
	Expt. (Ref. 28)	4.086	4.049	4.078	5.588	3.616	3.839	3.524	4.950	3.891	3.924	3.804	5.084	
B (GPa)	LDA	126.0	79.9	176.8	18.6	179.4	371.4	239.1	50.1	207.5	280.7	290.0		11.1
	PBE	86.0	73.6	127.0	16.7	131.0	328.0	185.9	39.5	157.3	232.6	241.0	55.2	−11.0
	PW91	88.6	71.7	128.8	17.3	131.7	326.1	187.7	40.2	158.1	230.0	241.6	56.0	−10.3
	AM05	106.2	81.6	159.8	16.9	153.9	370.1	215.9	44.4	189.0	272.6	281.6	59.1	2.1
	Expt. (Ref. 29)	104	76.7	173	17.6	138	355	184	44.7	195	289	267	59.6	
E_{coh} (eV)	LDA	3.56	3.72	4.22	2.03	4.54	9.08	5.97	3.51	4.95	6.90	7.33		26.6
	PBE	2.48	3.25	2.98	1.76	3.47	7.49	4.77	2.75	3.69	5.46	5.85	6.00	−0.8
	PW91	2.53	3.21	3.03	1.73	3.48	7.54	4.80	2.80	3.69	5.48	5.90	6.02	−0.2
	AM05	2.78	3.52	3.39	1.88	3.77	8.22		3.00	4.15	6.07	6.52	6.44	0.8
	Expt. (Ref. 30)	2.95	3.39	3.81	1.84	3.49	6.94	4.44	2.03	3.89	5.84	5.75	6.20	
n_{el} (Å^{-3})	LDA	0.678	0.190	0.655	0.054	1.000	0.645	0.989	0.138	0.699	0.670	0.673		
	PBE	0.610	0.182	0.605	0.048	0.921	0.620	0.915	0.126	0.646	0.635	0.635	0.374	
	PW91	0.613	0.181	0.604	0.047	0.922	0.617	0.917	0.126	0.645	0.631	0.634	0.373	
	AM05	0.662	0.186	0.651	0.245	0.984	0.643	0.968	0.133	0.692	0.673	0.676	0.397	

If only the description of the surface free energy is responsible for the discrepancy of the vacancy formation energy there should be an optimum x value x^{opt} for which all corrected $\tilde{E}_{\mathrm{f}}^{\mathrm{xc}}(x^{\mathrm{opt}})$ are identical. In practice this assumption is only approximately valid and we determine x^{opt} from a least-square minimization,

$$\sum_{ij}\left[\tilde{E}_{\mathrm{f}}^{\mathrm{xc}_i}(x^{\mathrm{opt}}) - \tilde{E}_{\mathrm{f}}^{\mathrm{xc}_j}(x^{\mathrm{opt}})\right]^2 \rightarrow \min, \qquad (2)$$

TABLE II. Formation energies, volumes of pure vacancies, and scaling factor for the area of vacancy internal surfaces in fcc metals. The literature data are taken from Refs. 28 (a), 31 (b), 32 (c), 33 (d), 34 (e), 1 (f), 35 (g), 36 (h), 37 (i), 38 (j), 39 (k), 40 (l), 41 (m).

		Ag	Al	Au	Ca	Cu	Ir	Ni	Pb	Pd	Pt	Rh	Th
E_{f} (eV)	LDA	1.03	0.57	0.62	1.22	1.29	1.79	1.66	0.54	1.44	0.99	2.00	–
	PBE	0.78	0.51	0.42	1.15	1.04	1.43	1.44	0.49	1.19	0.72	1.73	2.22
	PW91	0.76	0.43	0.39	1.13	0.99	1.37	1.38	0.47	1.16	0.69	1.64	2.15
	AM05	1.00	0.74	0.56	1.26	1.26	1.79	1.69	0.58	1.43	0.93	2.03	2.44
x		0.702	1.091	0.573	0.962	0.679	1.226	0.680	0.516	0.757	0.814	0.996	0.461
$\tilde{E}_{\mathrm{f}}$ (eV)	LDA	1.16	0.63	0.72	1.25	1.42	1.98	1.78	0.57	1.57	1.13	2.16	–
	PBE	1.09	0.66	0.67	1.26	1.37	1.90	1.75	0.56	1.51	1.06	2.13	2.41
	PW91	1.17	0.62	0.73	1.22	1.43	2.00	1.79	0.57	1.58	1.14	2.16	2.41
$H_{\mathrm{f}}^{\mathrm{exp}}$ (eV)	recommended value$^{\mathrm{a}}$	1.11 ±0.05	0.67 ±0.03	0.93 ±0.04		1.28 ±0.05		1.79 ±0.05	0.58 ±0.04		1.35 ±0.05		
	PAS	1.09–1.19$^{\mathrm{a}}$	0.60–0.82$^{\mathrm{a}}$	0.85–1.0$^{\mathrm{a,b}}$		1.04–1.49$^{\mathrm{a,b}}$		1.45–1.8$^{\mathrm{a}}$	0.47–0.70$^{\mathrm{a,d,e}}$	1.4–1.87$^{\mathrm{a,b,m}}$	1.26–1.44$^{\mathrm{a,b}}$		1.28±0.23$^{\mathrm{a}}$
	others experiments	1.06–1.3$^{\mathrm{a}}$	0.66–0.77$^{\mathrm{a}}$	0.94–0.98$^{\mathrm{a}}$		0.92–1.27$^{\mathrm{a}}$	1.79$^{\mathrm{l}}$	1.2–1.68$^{\mathrm{c}}$		1.5$^{\mathrm{k}}$	1.15–1.6$^{\mathrm{a}}$	1.7–2.5$^{\mathrm{a,f,l}}$	
$\Omega_{\mathrm{f}}/\Omega_0$	LDA	0.65	0.63	0.56	0.73	0.62	0.63	0.63	0.46	0.59	0.55	0.65	–
	PBE	0.70	0.65	0.56	0.79	0.72	0.64	0.65	0.60	0.63	0.55	0.66	0.62
	PW91	0.72	0.69	0.54	0.80	0.71	0.64	0.61	0.58	0.62	0.57	0.65	0.59
	AM05	0.68	0.64	0.59	0.84	0.69	0.64	0.62	0.53	0.61	0.55	0.65	0.52
	expt.		0.65,$^{\mathrm{h}}$ 0.62$^{\mathrm{h}}$	0.52,$^{\mathrm{i}}$ 0.85$^{\mathrm{a}}$		0.75$^{\mathrm{a}}$		0.80$^{\mathrm{a}}$			0.7$^{\mathrm{a}}$		

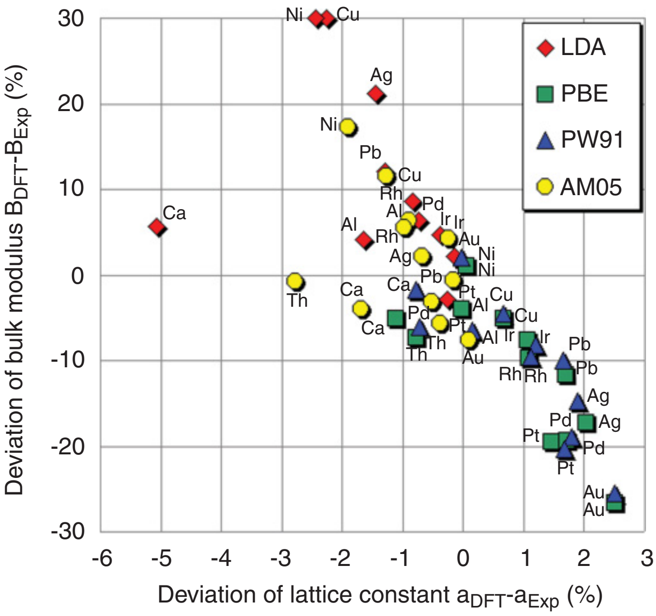

FIG. 2. (Color online) Deviation of calculated lattice constants and bulk modules from their respective experimental values for different metals and xc functionals.

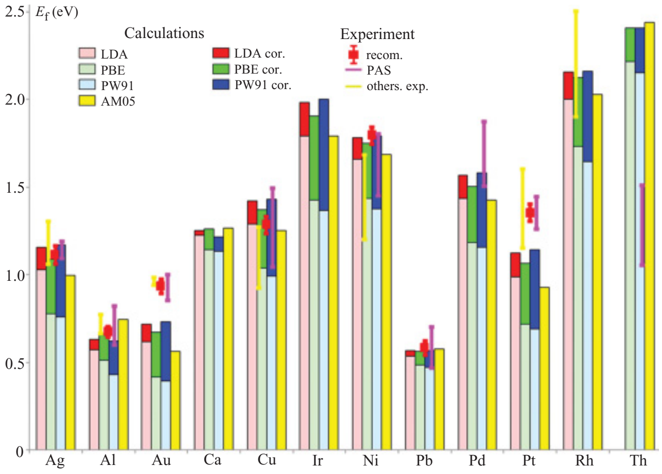

FIG. 3. (Color online) Calculated (bars from left to right: LDA, PBE, PW91, AM05) and experimental (lines) vacancy formation energies. The darker color bars show the corrected vacancy formation energies. The recommended value based on experimental data (Ref. 28) is shown by filled red squares together with error bars. The scatter in the experimental values from positron annihilation spectroscopy (PAS) (pink) and from others' techniques (yellow) is shown by segments.

where i and j run over the three xc functionals,- LDA, PBE, and PW91. We do not correct in this work the vacancy formation energy obtained by AM05 xc functional as the construction of this functional should yield a small error and the magnitude of $\Delta\sigma_{\mathrm{cor}}^{\mathrm{AM05}}(n_{\mathrm{el}}^{\mathrm{AM05}})$ is not known.

III. RESULTS AND DISCUSSION

In order to analyze the possible reason for a dependence on the xc functional, we investigate first if the deviations in the vacancy formation energies can be related to the performance of the xc functionals in describing bulk properties. To this end we first calculated the lattice constants and bulk modules for all 12 studied metals, which are presented in Table I. Due to the well-known overbinding in LDA,[43] we obtain for all fcc metals an underestimation of the lattice parameter by an average amount of 1.5% and an overestimation of the bulk modulus by averaged 11.1% for this functional (see Fig. 2). PBE (PW91) yields a better description of the lattice parameters with an average overestimation by 0.9% (0.9%), but its performance in predicting bulk modules is with averaged 11.0% (10.3%) underestimation similar to LDA. AM05 has the same performance in describing the lattice parameter as the GGA functionals (average underestimation is about 0.9%), however, it gives the best description of the bulk modulus overestimating it on average only by 2.1%. Thus AM05 gives the best description of these two parameters.

The overbinding of the LDA xc functional is also reflected in the calculated cohesive energies. The cohesion in LDA is on average 26.6% higher than in experiment. PBE (PW91) just slightly underestimates the cohesive energy by 0.8% (0.2%) and AM05 slightly overestimates it by 0.8%.

For the only ferromagnetic material in this set, Ni, we find an underestimated local magnetic moment of $0.55\mu_{\mathrm{B}}$ by LDA and values of $0.65\mu_{\mathrm{B}}$ by PBE, $0.63\mu_{\mathrm{B}}$ by PW91, and $0.63\mu_{\mathrm{B}}$ by AM05, which agree very well with the experimental value of $0.61\mu_{\mathrm{B}}$.[44] When performing the bulk calculations in Ni at the experimental lattice constant, we obtained a local magnetic moment of $0.62\mu_{\mathrm{B}}$, $0.65\mu_{\mathrm{B}}$, $0.63\mu_{\mathrm{B}}$, and $0.65\mu_{\mathrm{B}}$ by LDA, PBE, PW91, and AM05, respectively. Therefore the large discrepancy between the LDA result and the experimental magnetic moment is mostly related to the severe underestimation of the bulk lattice constant, which by itself is a consequence of LDA overbinding. The generality of this conclusion has already been discussed in Ref. 45 and subsequently for FeMn alloys in Ref. 46.

The calculated results for single vacancy formation energies and volumes together with experimental values are presented in Table II and in Fig. 3. The experimental data points are recommended values based on an analysis of all available experimental data.[28] As can be seen, the calculated vacancy formation energies are typically smaller than the experimental ones.

The vacancy formation energies obtained by using LDA and GGA differ significantly. The highest values for the vacancy formation energy are systematically found by using LDA and the lowest by PW91. The difference between these xc functionals is largest for metals with highest electronic density (≈0.4 eV for Ir and Rh). The variance (defined in this work as the difference between the maximal and minimal results for the xc functionals) is greatly reduced for metals with a lower number of valence electrons, such as Al, Ca, and Pb.

As already mentioned, LDA performs better for surfaces than GGA due to a cancellation of errors. This explains why the uncorrected LDA vacancy formation energies in Table II are closer to experiment and therefore higher than the GGA ones. The AM05 xc functional gives in most cases values for the vacancy formation energy that are close to those from LDA and therefore closer to experiment.

The relative vacancy formation volumes (Ω_f / Ω_0) differ for the xc functionals, but their variance exceeds slightly 0.1 only in the case of Pb (see Table II). We note that the variance of formation volumes shows no correlation with the variance of vacancy formation energies. For example, Ir, which exhibits a maximal difference between the vacancy formation energy in LDA and in PW91, gives formation volumes that almost coincide for all xc functionals. At the same time the largest difference in vacancy formation volumes is observed for Pb. Again this does not correlate with the very small variance in the vacancy formation energies.

Atomic relaxations in the first shell around a vacancy, which determine the internal surface of a vacancy, are small and inward. They exceed only in rare cases 0.1 Å (in our set only for Pt and Th). The reason is that large relaxations are hard to realize in close-packed fcc structures. The difference between all xc functionals normally does not exceed 0.01 Å, and can thus not explain the large difference between the formation energies of vacancies. The impact of the incorrect description of the lattice parameter on the vacancy formation energies has been considered previously[7] and found to be small and not sufficient to explain the discrepancies between xc functionals.

An overestimation of the cohesive energy by LDA could be another reason for higher LDA values of the vacancy formation energy. Indeed we observe a linear correlation between the vacancy formation energy and the cohesive energy obtained by different xc functionals for the same element (see Fig. 4). The slopes of this correlation lie mostly around 0.2–0.3 with the most dramatic outlier for Th (0.76). A simple bond cutting model, which works well for covalent metals, gives a value of 2 but largely overestimates this slope. A more realistic metals-oriented tight-binding model[47] gives a slope of 1/3, which for most metals agrees with our calculations. A similar relation has empirically been obtained earlier by Gorecki.[48] The fact that for some elements the vacancy formation energy lies below this slope could be a consequence of local relaxations. Nevertheless, despite the fact that the LDA cohesive energies are always higher than the experimental ones, LDA vacancy formation energies are normally lower than in experiment.

The vacancy formation energy in magnetic materials differs from the value obtained in the same material treated nonmagnetically. For example, the vacancy formation energy in magnetic fcc Fe is 0.6 eV smaller than in nonmagnetic one.[49] Therefore one might expect a correlation between the vacancy formation energy and the magnetization for different xc functionals. Apparently, this is not the case, since for Ni the PW91 and AM05 xc functionals give the same local magnetic moment of $0.63\mu_B$, but the difference in the vacancy formation energy attains 0.32 eV. Furthermore, we have already shown that the underestimation of the local magnetic moment in LDA is mostly due to the underestimation of the equilibrium lattice parameter. However, this effect alone cannot explain the difference in the vacancy formation energy using different xc functionals.[7]

According to the previous discussion we now consider the only remaining candidate for the variance in the vacancy formation energy obtained by xc functionals: the different description of the internal surface of a vacancy. If this is the principal reason for different values of the vacancy formation energy their variance should be greatly reduced after applying the correction scheme presented above.

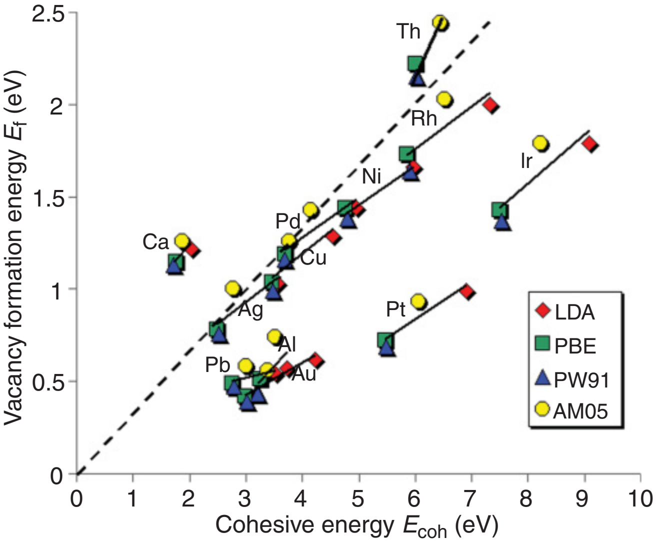

FIG. 4. (Color online) Vacancy formation energies with respect to cohesive energies for different metals and xc functionals. Solid lines provide linear regressions for the same element, the dashed black line corresponds to the relation $E_{vac} = 1/3 E_{coh}$ (see text).

The corrected vacancy formation energies ($\tilde{E}_f^{xc}$) are presented in Table II and in Fig. 3. After the introduction of our correction scheme the difference between two exchange-correlation approximations (LDA and GGA) is dramatically reduced. The maximal variance of the corrected results is only 0.1 eV (instead of 0.42 eV for noncorrected values). Furthermore, the maximal difference to the AM05 results is also reduced from 0.42 to 0.21 eV. The agreement of the corrected vacancy formation energies with experiment becomes better, too. The uncorrected values were in some cases largely underestimated compared to experiment. This discrepancy attained as much as 0.75 eV for Pt. Using the correction the obtained vacancy formation energies lie generally closer to the values obtained by PAS (which is usually believed to be the most reliable experimental technique[1]). We should notice, however, that not only the formation energies but even the vacancy concentrations are obtained indirectly by this technique. Therefore the experimental formation energies (which are supposed to be exponentially related to the vacancy concentration) are not only sensitive to the purity of the experimental setup, but also to the quality of the models for positron trapping and the fitting procedure. To determine the vacancy formation energy in Th, Kim *et al.*[50] used a standard trapping model[51] based on several assumptions and additionally made some assumptions for the fitting coefficients of it. This could be the reason why the ratio between their value for the vacancy formation energy and the activation energy of self-diffusion was found to be too small compared to the typical value found in most metals.

The inability of the chosen xc functionals to account for Van der Waals interaction could also be a reason for the discrepancy between the calculated and experimental vacancy formation energies in Au. Mahanty and Taylor[52] theoretically investigated the effect of van der Waals interaction on the vacancy formation energy in Cu, Ag, and Au. They found that the van der Waals contribution to the vacancy formation energy is 15% for Cu, 30% for Ag, and 50% for Au. The addition of these values to our results leads to overestimated vacancy formation energies compared to experiment. Therefore the amount of van der Waals contribution to the vacancy formation energy found by Mahanty and Taylor seems to be overestimated. Nevertheless, the fact that the largest underestimation of the vacancy formation energy should be observed in Au is in agreement with our findings. Furthermore, fully relativistic effects (as spin-orbit coupling), which are not considered in this work, could be non-negligible for $5f$ elements like Th. The effect of spin-orbit coupling has been studied by Nordström *et al.*[53] in actinides and it was found that among all light actinides the inclusion of full relativity has the strongest effect on the lattice parameter in Th. Therefore full relativity could subsequently change the vacancy formation energy in Th. Finally, we note that the vacancy formation energies presented in this work are obtained at 0 K, whereas experiment is performed at high temperatures to ensure equilibration. Therefore the discrepancy with experiment can be also related to extrapolating experimental data to $T = 0$ K.[3]

IV. CONCLUSION

Based on a large set of 12 fcc metals we discuss the performance of popular xc functionals (LDA, PBE, PW91, and AM05) in predicting vacancy formation energies. Our results show a strong dependence on the choice of the xc functional. Analyzing the origin of the discrepancy we find that bulk material properties (lattice constant, bulk modulus, and cohesive energy) have only a minor impact on the xc dependence of the vacancy formation energy. Furthermore, differences in vacancy geometry (local relaxations and vacancy formation volume) and differences in magnetic moments are also unable to explain this discrepancy.

We conclude that the principal reason for the large dependency of the vacancy formation energies on the choice of the xc functionals lies in the different description of the internal vacancy surface. We propose a modified version of the postcorrection scheme,[16] which allows us to align vacancy formation energies from all xc functionals. The so-obtained vacancy formation energies largely reduce deviation between the various functionals and are also in very good agreement with experiment.

We note that the scheme proposed here is general and can also be applied to defect structures in which the internal free surface cannot be easily determined, e.g., for interstitial atoms, self-diffusion barriers, voids, dislocations, grain boundaries, etc.

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[1] Y. Kraftmakher, Phys. Rep. **299**, 79 (1998).
[2] K. Takai, H. Shoda, H. Suzuki, and M. Nagumo, Acta Mater. **56**, 5158 (2008).
[3] B. Grabowski, T. Hickel, and J. Neugebauer, Phys. Status Solidi B **248**, 1295 (2011).
[4] P. A. Korzhavyi, I. A. Abrikosov, B. Johansson, A. V. Ruban, and H. L. Skriver, Phys. Rev. B **59**, 11693 (1999).
[5] K. Carling, G. Wahnström, T. R. Mattsson, A. E. Mattsson, N. Sandberg, and G. Grimvall, Phys. Rev. Lett. **85**, 3862 (2000).
[6] T. R. Mattsson and A. E. Mattsson, Phys. Rev. B **66**, 214110 (2002).
[7] L. Delczeg, E. K. Delczeg-Czirjak, B. Johansson, and L. Vitos, Phys. Rev. B **80**, 205121 (2009).
[8] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
[10] J. P. Perdew, *Electronic Structure of Solids* (Akademie Verlag, Berlin, 1991), p. 11.
[11] A. J. Hatt, B. C. Melot, and S. Narasimhan, Phys. Rev. B **82**, 134418 (2010).
[12] S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).
[13] L. M. Almeida, J. P. Perdew, and C. Fiolhais, Phys. Rev. B **66**, 075115 (2002).
[14] R. Armiento and A. E. Mattsson, Phys. Rev. B **72**, 085108 (2005).
[15] A. E. Mattsson, R. Armiento, J. Paier, G. Kresse, J. M. Wills, and T. R. Mattsson, J. Chem. Phys. **128**, 084714 (2008).
[16] A. E. Mattsson, R. R. Wixom, and R. Armiento, Phys. Rev. B **77**, 155211 (2008).
[17] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[18] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[19] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).
[20] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[21] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[22] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[24] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[25] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[26] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).
[27] F. Birch, Phys. Rev. **71**, 809 (1947).
[28] P. Ehrhart, P. Jung, H. Schultz, and H. Ullmaier, *Atomic Defects in Metals* (Springer-Verlag, Berlin, 1991), Chap. Group III.
[29] M. A. Shtremel, *Strength of Alloys, Part 1. Lattice Defects* (MISIS, Moscow, 1999).
[30] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (John Wiley & Sons, Inc, New York, 2005).
[31] H.-E. Schaefer, Phys. Status Solidi A **102**, 47 (1987).
[32] E. H. Megchiche, S. Pérusin, J.-C. Barthelat, and C. Mijoule, Phys. Rev. B **74**, 064111 (2006).

[33] B. T. A. McKee, W. Triftshäuser, and A. T. Stewart, Phys. Rev. Lett. **28**, 358 (1972).
[34] S. C. Sharma, S. Berko, and W. K. Warburton, Phys. Lett. A **58**, 405 (1976).
[35] A. Seeger, J. Phys. F **3**, 248 (1973).
[36] R. M. Emrick and P. B. McArdle, Phys. Rev. **188**, 1156 (1969).
[37] H. H. Grimes, J. Phys. Chem. Solids **26**, 509 (1965).
[38] R. M. Emrick, Phys. Rev. B **6**, 1144 (1972).
[39] J. Emsley, *The Elements* (Clarendon, Oxford, 1991).
[40] F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals* (North-Holland, Amsterdam, 1988).
[41] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).
[42] A. E. Mattsson, R. Armiento, P. A. Schultz, and T. R. Mattsson, Phys. Rev. B **73**, 195123 (2006).
[43] B. Grabowski, T. Hickel, and J. Neugebauer, Phys. Rev. B **76**, 024309 (2007).
[44] *Handbook of Chemistry and Physics*, edited by D. Lide (CRC, Boca Raton, 1995).
[45] A. V. Ruban and I. A. Abrikosov, Rep. Prog. Phys. **71**, 046501 (2008).
[46] M. Ekholm and I. A. Abrikosov, Phys. Rev. B **84**, 104423 (2011).
[47] T. Korhonen, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **51**, 9526 (1995).
[48] T. Gorecki, Z. Metallkd. **65**, 426 (1974).
[49] R. Nazarov, T. Hickel, and J. Neugebauer, Phys. Rev. B **82**, 224104 (2010).
[50] S. M. Kim, J. A. Jackman, W. J. L. Buyers, and D. T. Peterson, J. Phys. F **14**, 2323 (1984).
[51] R. N. West, *Positrons in Solids* (Springer, New York, 1979), pp. 89–144.
[52] J. Mahanty and R. Taylor, Phys. Rev. B **17**, 554 (1978).
[53] L. Nordström, J. M. Wills, P. H. Andersson, P. Söderlind, and O. Eriksson, Phys. Rev. B **63**, 035103 (2000).