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Helium, neon and argon in copper studied with the effective medium theory

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Abstract. Two-component effective medium theory (EMT) is applied to calculate binding, migration and dissociation energies of helium, neon and argon in bulk copper. Interstitial helium and neon prefer octahedral sites whereas argon sits about 0.5 Å off-centred in the octahedral site. Helium has the smallest migration energy, but, surprisingly, the migration energy of argon is smaller than that of neon. A vacancy in copper can bind three helium atoms or two neon atoms, but only one argon atom. Results are compared with those obtained from thermal desorption measurements.

1. Introduction

Effective medium theory (EMT) has been shown to be a good tool to investigate chemical binding energies between different atomic species [1–5]. It has been successfully applied to a wide variety of different problems, including bulk properties of metals, surface energy and reconstruction, adsorption and desorption phenomena etc. EMT is simple enough for large-scale molecular dynamics or Monte Carlo simulations and still it contains essential features of metallic bonding which cannot be described with pair potentials. The basic idea behind the EMT is to relate the real system to a homogeneous electron gas and calculate the energy of an atom embedded in this electron gas. This problem can be solved accurately with the density functional theory [2] using the local density approximation [6, 7].

We have applied a two-component EMT to gas–metal and defect–gas interactions in bulk copper. The two-component EMT allows us to study the relaxation of atoms around the impurity as well as impurity–impurity interactions. The results can be used in analysing thermal desorption spectra of rare gases embedded in copper.

In section 2 we give a short description of the theory and in section 3 we will give the detailed parameters of the two-component model. Results for the migration and binding energies as well as relaxation of host atoms around the impurity are given in section 4. Discussion and conclusions are given in section 5.

2. Effective medium theory

The key idea of EMT is to calculate the energy of an atom in a real metal by comparing it to the energy of a simpler system [2]. Usually the reference system is assumed to be a homogeneous electron gas. In the following we will give a only short summary of the basic theory, relevant to the determination of the parameters needed. A more complete derivation is given in [2] and [3].

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The total energy of the system of atoms is written as the sum of three terms

$$E_{tot} = \sum_i E_{c,i}(\bar{n}_i) + \Delta E_{AS} + \Delta E_{1\text{-el}} \tag{1}$$

where $E_{c,i}(\bar{n}_i)$ is the so-called cohesive function for atom i in an effective density $\bar{n}_i$, ΔE_{AS} is an atomic sphere correction and $\Delta E_{1\text{-el}}$ a one-electron energy correction.

The cohesive function $E_{c,i}$ is derived from the electronic structure and energetics of an atom embedded in a homogeneous electron gas. The cohesive function is usually expressed in the form of a third-order polynomial [2]

$$E_c(\bar{n}) = E_0 + E_2\left(\frac{\bar{n}}{n_0} - 1\right)^2 + E_3\left(\frac{\bar{n}}{n_0} - 1\right)^3 \tag{2}$$

where E_i are parameters and n_0 is the density at the minimum of the E_c function. This equation is suitable for most elements. However, in the case of noble gases the E_c function does not have a clear minimum and for He, Ne and Ar it is better to use a simple polynomial of the form

$$E_c(\bar{n}) = E_1\bar{n} + E_2\bar{n}^2 + E_3\bar{n}^3. \tag{3}$$

Figure 1 shows these E_c-curves for helium, neon, argon and copper as a function of density parameter r_s. Gas atoms do not have minima in the E_c-curve. This means that they interact repulsively with all materials. In the case of neon and argon the curves have only slight curvature and still there are no minima. On the other hand, the cohesive function for metal atoms is totally different showing a clear minimum at the optimum density.

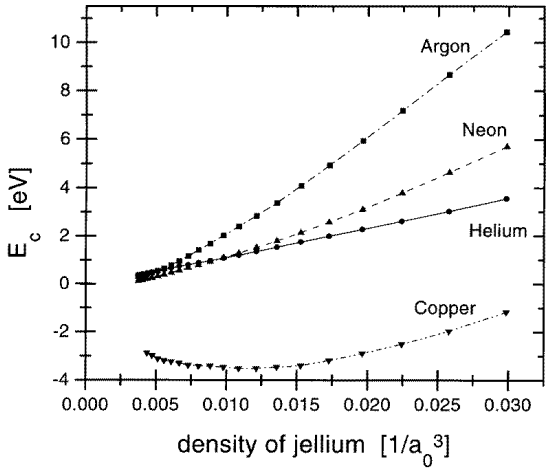

Figure 1. Calculated E_c-curves for helium, neon, argon and for copper as a function of electron gas density.

The second term in equation (1) gives the atomic sphere correction which comes purely from electrostatics. If interacting atoms are identical this correction is approximated as

$$\Delta E_{AS}^{MM} = \alpha \sum_i \left\{ \bar{n}_i - \frac{n_0}{12} \sum_{j \neq i} \mathrm{e}^{-\eta(r_{ij}\ \beta - s_0)} \right\} \tag{4}$$

where r_{ij} is the distance between atoms i and j, α and η parameters and β a geometrical factor.

If the system has two different atoms the correction term is usually described with the positive overlap region only. We denote by A the impurity (a noble gas atom in our case) and by M a host metal atom. The atomic sphere correction will then be [1]

$$\Delta E_{AS}^{AM} = -\int_{\Omega} \mathrm{d}^3\boldsymbol{r}\left[\Delta n^M(\boldsymbol{r})\Delta\phi^A(\boldsymbol{r}) + \Delta n^A(\boldsymbol{r})\Delta\phi^M(\boldsymbol{r})\right] \tag{5}$$

where Ω is the overlap volume, Δn is induced density and $\Delta\phi$ is induced electrostatic potential which is calculated from the induced density. It is obvious that this approximation gives an upper limit to the repulsion since holes are ignored totally. The above integral is calculated with several jellium densities and, respectively, with several induced potential and density profiles, and the results are fitted to exponentially decaying form

$$\Delta E_{AS}^{A,M} = V^{A,M}\Omega_{ik}\exp\left(-\phi_M s_i - \phi_A s_k - \phi_R r_{ik}\right) \tag{6}$$

where Ω_{ik} is the overlap volume of the two atoms, ϕ_M, ϕ_A and ϕ_R are fitting parameters, s_i and s_k are values for the neutral sphere radii and r_{ik} is the distance between the gas and the host-metal atoms in question.

The last term in equation (1), the one-electron energy term, is not important when dealing with inert gas atoms and with bulk copper [1, 2, 5]. Consequently, it will be neglected here.

3. Detailed equations and parameters for the two-component EMT

The equations for the two-component EMT are essentially the same as presented in [1]. For completeness we repeat the equations relevant to our study:

$$\begin{aligned}
\bar{n}_i^{Cu} &= n_0^{Cu}\exp\left[-\eta^{Cu}(s_i - s_0^{Cu})\right] = \sum_{Cu}\frac{n_0^{Cu}}{12}\exp\left[\eta_1^{Cu}(s_i - s_0^{Cu}) - \eta_2^{Cu}(r_{ij} - \beta s_0^{Cu})\right] \\
\bar{n}_k^{Ads} &= n_0^{Ads}\exp\left[-\eta^{Ads}(s_k - s_0^{Ads})\right] = \sum_{Ads}\frac{n_0^{Ads}}{12}\exp\left[\eta_1^{Ads}(s_k - s_0^{Ads}) - \eta_2(r_{kl} - \beta s_0^{Ads})\right] \\
&\quad + \sum_{Cu}\tilde{n}_0^{Cu}\exp\left[\tilde{\eta}_1^{Cu}(s_k - \tilde{s}_0^{Cu}) - \tilde{\eta}_2^{Cu}(r_{kj} - \tilde{r}_0)\right] \\
E_{c,i}^{Cu} &= E_0^{Cu} + E_2^{Cu}\left(\frac{\bar{n}_i^{Cu}}{n_0^{Cu}} - 1\right)^2 + E_3^{Cu}\left(\frac{\bar{n}_i^{Cu}}{n_0^{Cu}} - 1\right)^3 \\
E_{c,k}^{Ads} &= E_1\bar{n} + E_2\bar{n}^2 + E_3\bar{n}^3 \\
\Delta E_{AS} &= \sum_{Cu}\left\{\alpha^{Cu}\left(\bar{n}_i - \frac{n_0^{Cu}}{12}\sum_{Cu}\exp\left[-\eta(r_{ij}\ \beta - s_0^{Cu})\right]\right)\right. \\
&\quad \left. + \sum_{Ads} V^{Ads,Cu}\Omega_{ik}\exp\left[-\phi_{Cu}s_i - \phi_{Ads}s_k - \phi_R^{Ads,Cu}r_{ik}\right]\right\} \\
E_{Tot} &= \sum_{Cu}E_{c,i}^{Cu} + \sum_{As}E_{c,k}^{Ads} + \Delta E_{AS}.
\end{aligned} \tag{7}$$

The parameters for pure materials are given in table 1 and the additional parameters needed for the two-component systems are given in table 2. For determining the parameters the atoms were embedded in a homogeneous electron gas and the induced density and energetics

were calculated self-consistently. Results obtained with different electron gas densities were fitted to (2)–(7). This fitting is not straightforward since it depends on the range where the functions are needed (the fitting is always better around the fitting centre). Several different minimization methods were used in order to get the best fit.

Table 1. Parameters of the effective medium theory for helium, neon and argon in bulk copper. Some of the parameters have been taken from [2].

Parameter	Helium	Neon	Argon	Copper
E_0				−3.5620
E_1	98.8930	33.9120	44.6330	
E_2	1412.4	9153.2000	20 375.0000	1.2870
E_3	−22 747.0000	-1.2787×10^5	-3.3231×10^5	−0.2950
n_0	0.020 95	0.020 95	0.020 95	0.011 30
s_0	1.6459	2.0450	2.4500	2.5860
η	2.8760	3.4360	2.4150	2.4870
η_1	0.436 00	0.423 66	0.518 30	0.234 00
$V^{(Ads,Cu)}$	284.8400	2070.1600	395.8769	
$\phi_{Cu}^{(Ads,Cu)}$	0.6801	2.3347	1.4637	
$\phi_{Ads}^{(Ads,Cu)}$	0.669 50	1.797 10	−0.013 89	
$\phi_R^{(Ads,Cu)}$	1.581 90	0.328 70	1.594 80	

Table 2. Parameters of two-component EMT for helium, neon and argon in bulk copper.

Parameter	Helium	Neon	Argon
$\tilde{n}_0^{Cu}$	0.004 391	0.004 656	0.006 902
$\tilde{n}_0^{Ads}$	0.001 203	0.003 334	0.007 072
$\tilde{s}_0{}^{(Cu,Ads)}$	2.50	2.50	2.50
$\tilde{s}_0{}^{(Ads,cu)}$	1.60	2.00	2.40
$\tilde{\eta}_1{}^{Cu}$	0.439 100	0.966 530	0.979 900
$\tilde{\eta}_2{}^{Cu}$	1.713 900	1.890 410	1.907 700
$\tilde{\eta}_1{}^{Ads}$	0.818 300	0.581 640	0.589 700
$\tilde{\eta}_2{}^{Ads}$	1.749 500	1.746 780	1.610 950

4. Results

4.1. Interstitial sites and migration

All calculations reported in this paper are so-called relaxation calculations. This means that the gas atom is placed in an appropriate site in an otherwise perfect lattice and all atoms except a fixed boundary layer are relaxed according to Newton's equation of motion in a force field determined by the EMT. It is not easy to express forces in closed form since the equations of the potential energy have to be solved iteratively. In the present work we have used a four-point central difference scheme for force calculation.

First the migration energies for helium, neon and argon in bulk copper were calculated. For this calculation we generated a lattice which has 1687 mobile bulk atoms and 769 atoms in the immobile boundary layer. The substitutional gas atom was placed first in the octahedral site near the centre of the lattice and then it was moved with small steps to another octahedral site. At each step all other atoms except the atoms of the fixed boundary layer and the gas atom in question were relaxed to minimize the total energy. The same calculation was repeated by moving the gas atom from a tetrahedral site to the nearest octahedral site.

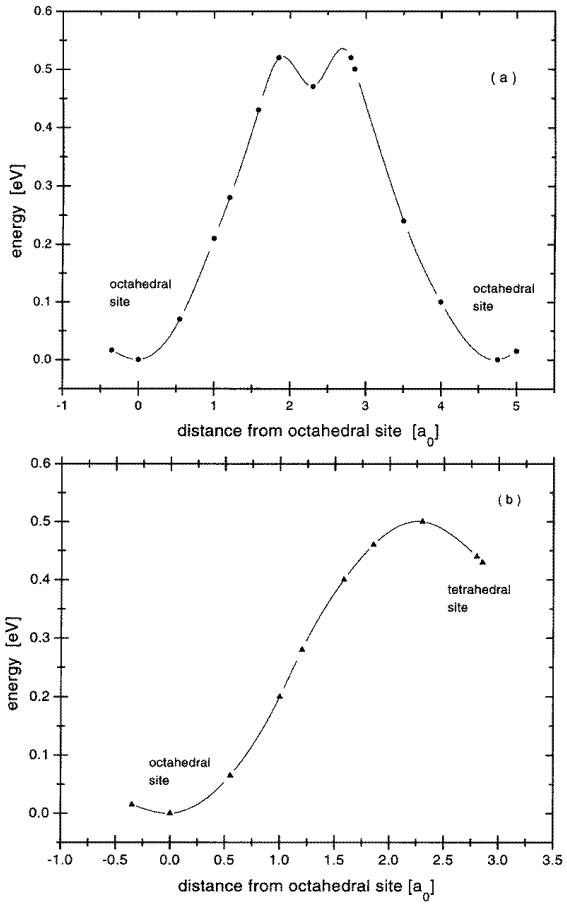

Figure 2. Energy of a helium atom along diffusion path between two octahedral sites (a) and from an octahedral site to a tetrahedral site (b).

Figure 2 shows results for helium in copper. The preferential interstitial site for helium is the octahedral site. The energy for the tetrahedral site is about 0.4 eV higher. The migration energy from octahedral site to octahedral site is about 0.5 eV. The same barrier height is obtained both for the direct diffusion and via the tetrahedral site.

Results for neon and argon are shown in figure 3. In the case of neon the preferred diffusion path goes through the tetrahedral site, the migration energy being 0.8 eV, which is 0.1 eV less than a direct jump from octahedral to octahedral site. The preferred site is

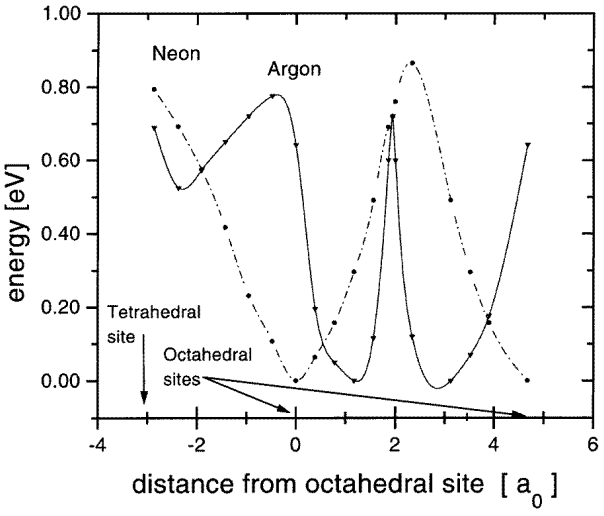

Figure 3. Energies of neon and argon along the diffusion path from a tetrahedral site to an octahedral site and another octahedral site.

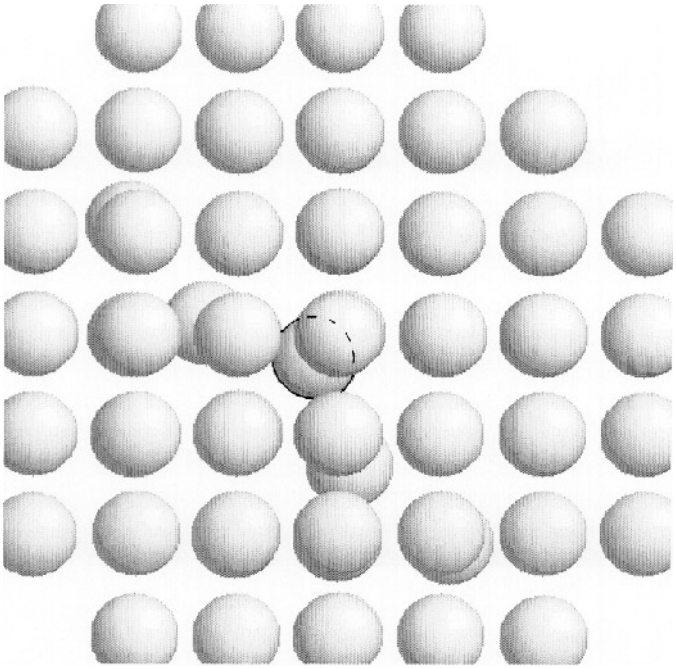

Figure 4. Lattice relaxation around an argon impurity in the minimum-energy site (off-centred octahedral site). The argon impurity is indicated with a black circle. The viewing direction is along the (100)-axis.

again in the centre of the octahedral site. In the case of neon the tetrahedral site is not even a local minimum.

Argon behaves in copper very differently from helium or neon. The preferred site is

not in the centre of the octahedral site but clearly off-centred, as seen in figure 3. In the tetrahedral site argon also has a local minimum, but also this minimum is off-centred. The migration energy is 0.7 eV, i.e. in between the values of helium and neon. The diffusion path goes directly from one octahedral site to another octahedral site. The route through a tetrahedral site has a slightly higher migration energy.

Figure 4 shows the minimum-energy site for argon in copper. As can be seen, the configuration is not symmetric but argon pushes two nearest atoms away from their normal lattice sites. The relaxation of copper atoms around the impurity when the argon atom is in the centre of the interstitial site is given in table 3.

Table 3. Calculated relaxations of copper atoms around a gas atom impurity.

		Octasite (%)	Tetrasite (%)	In vacancy (%)
	Δd_n	+16.8	+32.0	+0.7
Argon	Δd_{nn}	+1.3	+0.2	—
	Δd_{nnn}	+0.02	+0.0	—
Neon	Δd_n	+11.3	+20.9	+0.6
	Δd_{nn}	+0.0	+0.0	—
Helium	Δd_n	+5.1	+8.0	+0.6

The non-monotonic behaviour from helium to argon can be traced back to the screening properties of the rare gas atoms in electron gas. In the case of neon the screening has a surprisingly short range. The parameter η describing the decay of the electron density is larger in neon than in helium or argon.

Earlier calculations and computer simulations for the helium migration energy are in good agreement with our results [8–11]. Our results are only slightly lower than the previous predictions. However, contrary to earlier calculations our results indicate that in the case of helium the migration energy is the same for the octahedral–octahedral jump and for the octahedral–tetrahedral–octahedral jump. Perturbed angular correlation measurements have suggested that the migration energy for helium might be considerably smaller than our result [12].

4.2. Trapping at vacancies

Rare gas atoms in pre-existing vacancies were calculated in a similar fashion as the interstitial gas atoms. The gas atom was moved from the centre of the vacancy to the nearest and next-nearest octahedral sites. Again, for each site of the helium atom the copper atom positions were allowed to relax. Calculations were repeated by moving the gas atom from the centre of the vacancy to the nearest tetrahedral site and from there to the next-nearest octahedral site.

The results for the binding energies and dissociation energies are given in table 4. The binding energy (trapping energy) is defined to be energy change when one gas atom is moved from the equilibrium site in the vacancy to the equilibrium site in an octahedral interstitial site (far away from the vacancy). The dissociation energy is defined as the height of the potential barrier when the atom moves out of the vacancy. Neon has the largest binding and dissociation energies of the three gases studied. This is again related to the size of the neon atom in metallic surroundings (large η-parameter).

Table 4. Calculated energies: E_M is the migration energy in bulk copper, $E_{B,i}$ is the binding energy of the gas atom in a vacancy and $E_{D,i}$ is the dissociation energy of the gas atom from the vacancy, when the vacancy has i gas atoms. E_V^F is the vacancy formation energy.

	Helium	Neon	Argon	Copper
E_M (eV)	0.50	0.80	0.70	
E_B (eV)	1.67	3.00	2.18	
$E_{B,2}$ (eV)	1.19	1.40	—	
E_D (eV)	2.17	3.80	2.87	
$E_{D,2}$ (eV)	1.75	1.90	—	
$E_{D,3}$ (eV)	1.45	—	—	
E_V^F (eV)	—	—	—	1.45

It is well known that a metal vacancy can trap several helium atoms. We calculated the binding energy of the second and third helium atoms as follows. One helium atom was moved out from the vacancy while other helium atoms and copper atoms were allowed to relax. The results for helium are shown in figure 5. The binding energy of the helium atom is defined as the energy difference between the relaxed positions in the vacancy and in the interstitial octahedral site. We also define the dissociation energy as the energy difference from the relaxed position in the vacancy to the highest point at the diffusion barrier. The results are given in table 4.

In the case of neon, the vacancy can trap two atoms and in the case of argon only one atom. This is natural since the size of these atoms is larger than that of a helium atom. For example, the radius of the neutral sphere s_0 for argon is about the same as for copper (see table 1).

In thermal desorption experiments the measured quantity is just the dissociation energy. Experimental estimates of the dissociation energies for the helium–copper system are $E_{D,He} = 2.1$ eV, $E_{D,2He} = 1.3$ eV and $E_{D,3He} = 0.9$ eV [13]. These values are somewhat smaller than the calculated values. No experimental results exist for neon and argon in copper.

For comparison, we have also calculated the vacancy formation energy for copper. The result, $E_f^v = 1.45$ eV, is in reasonable agreement with the experimental value of 1.28 eV [14]. Relaxation around a vacancy is very small; the nearest atoms relax outwards by about 0.6%. Due to the long-range relaxation both the vacancy formation energy and the relaxation of the nearest neighbours depend slightly on the size of the mobile atoms of the lattice, even when we have nearly 2000 mobile atoms.

5. Discussion and conclusions

The main results obtained in this work are the migration energies of rare gases in bulk copper, $E_M^{He} = 0.5$ eV, $E_M^{Ne} = 0.8$ eV and $E_M^{Ar} = 0.7$ eV, and dissociation energies from vacancies, $E_D^{He} = 2.17$ eV, $E_D^{Ne} = 3.8$ eV and $E_D^{Ar} = 2.87$ eV. In the case of helium in copper our result for migration energy seems to be slightly lower than other calculated results [8–11]. This is true also for trapping and dissociation results for helium in copper [8–11, 15]. When compared to desorption experiments, our result for the helium dissociation energy is in perfect agreement with them [13, 16]. However, in the case of two and three helium atoms in a copper vacancy, our results are higher than the measured ones.

Experimental migration energies for argon and neon in copper have not been reported

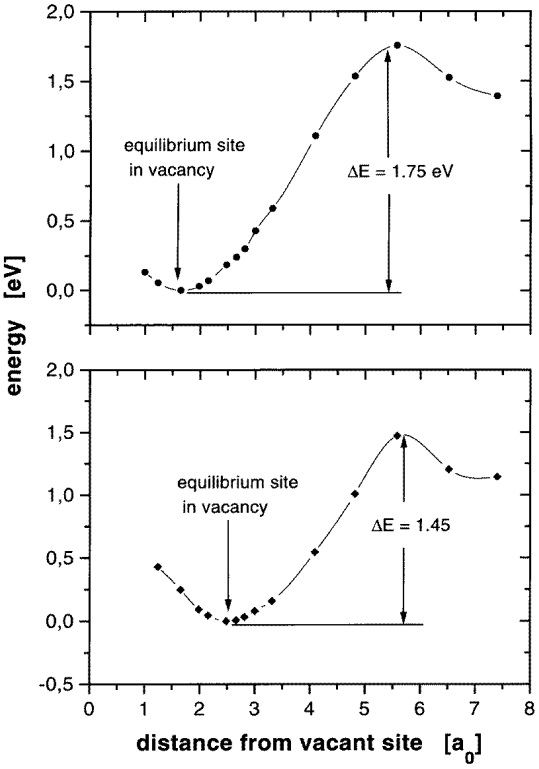

Figure 5. Energy of a helium atom along the dissociation path when the vacancy is originally filled with two (upper panel) and three (lower panel) helium atoms.

in the literature. The obtained dissociation energy for the neon is quite high, much higher than that of argon. Indeed desorption experiments shows that in some cases neon peaks appear at slightly higher temperatures than argon peaks [13].

It seems that double-component effective medium theory is suitable for studying rare gas impurities in metals. However, it is expected that the effective medium theory gives slightly too large values for energies since the atomic sphere correction part includes only the positively overlapping parts of atoms and the 'holes' are ignored.

Acknowledgment

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