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Solute–vacancy interactions in Cu and Ag

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Abstract. We present local-spin-density-functional calculations for the interaction energies of vacancies with 3d and 4sp impurities in Cu as well as with 4d and 5sp impurities in Ag. The calculations are based on the jellium model and first-order perturbation theory, thus enabling an interpretation of the interaction in purely electrostatic terms. The results are in agreement with those obtained by first-principles calculations and confirm the experimentally known trends.

1. Introduction

The interaction of point defects with vacancies in solids is an active area of theoretical and experimental investigations because it is important for the understanding of diffusion in dilute alloys.

Calculations dealing with the solute–vacancy binding energy in simple metals have been performed first by Lazarus [1] and Le Claire [2]. They considered the noble metals within the jellium model and employed the Thomas–Fermi approximation to describe the screening of the impurity.

As an improvement to this approach, Blandin and co-workers [3] and Gupta [4] have taken into account the oscillatory behaviour of the screening, using the asymptotic form of Friedel [5] oscillations determined by some reasonable assumptions for the impurity phase shifts. Their results for the solute–vacancy interaction in noble metal hosts roughly reproduce the experimental trends.

Subsequent calculations based on pseudopotential theory [6, 7] have a restricted range of applicability. Apart from the fact that the pseudopotential method is applicable only to simple metal solutes in simple metal hosts, the results obtained are very sensitive to the choice of the pseudopotential. Application of this method even to impurities with a small valence difference seems to be problematic [7], and even more so the treatment of vacancies [8].

Calculations performed within the framework of the tight-binding method [9] had a limited success. Despite the fact that this method enables physical insight into various electronic structure problems, it is restricted to transition metals. Moreover, the method contains a number of adjustable parameters which are difficult to determine.

Recently, Klemradt *et al* [10, 11] reported an extensive study of the solute–vacancy interaction by performing *ab initio* total energy calculations for various impurity–

vacancy complexes in Cu, Ni, Ag and Pd hosts using the Korringa–Kohn–Rostoker (KKR) Green function method.

In this paper we show that the jellium model together with first-order perturbation theory can indeed explain the trends for the interaction energies in noble metal hosts and gives results in agreement with the results of *ab initio* calculations and with experimental data, provided that the calculations are performed accurately and consistently. The satisfactory results found in earlier jellium calculations [1–4] are more or less accidental and due to error cancellations of the different unreliable approximations involved. Because of the simplicity of the model we can readily gain physical insight of the solute–vacancy interaction.

2. Computational method

We first consider a substitutional impurity in a simple metal. The band-structure effects associated with the host matrix are ignored and a jellium of appropriate density $\bar{\rho} = 3Z_0/4\pi r_s^3$ is introduced. Z_0 is the valence of the host, being equal to unity if we consider the noble metals (Cu and Ag in this work) as jellia and r_s is the radius of the host atomic sphere. In this paper, Rydberg atomic units are used.

The substitutional impurity of atomic number $Z_{\text{imp}} = Z_0 + \Delta Z$ is embedded in a spherical hole of radius r_s in the positive background density. The spherically symmetric perturbing potential is considered to extend up to a distance S around the impurity, taken at the origin of coordinates. For a given spherically symmetric total electron density

$$\rho(r) = \sum_{\sigma} \rho_{\sigma}(r) \quad (1)$$

where ρ_{σ} is the electron density for a spin direction σ , the one-electron effective potential is written within the framework of density-functional theory [12] as

$$V_{\sigma}(r) = V_c\{\rho(r)\} + V_{xc,\sigma}\{\rho_{\sigma}(r)\}. \quad (2)$$

V_c is the potential energy of an electron in the electrostatic field created by the total charge distribution within a sphere of radius S around the impurity. An explicit expression for V_c has been given in a previous paper [13]. The term $V_{xc,\sigma}$ describes exchange and correlation effects, which are taken into account through the local-spin-density approximation of von Barth and Hedin [14] with the parametrization proposed by Moruzzi *et al* [15].

We employ the frozen-core approximation according to which the core electron density $\rho_c(r)$ is equal to that of an isolated impurity atom. The electron density associated with the valence states, which extends from a lower value E_{inf} to the Fermi level E_F and includes possible shallow bound states, is calculated from the Green function

$$\rho_{v,\sigma}(r) = -\frac{1}{\pi} \text{Im} \left(\int_{E_{\text{inf}}}^{E_F} dE \Delta G_{v,\sigma}(r, r; E) \right) + \bar{\rho}. \quad (3)$$

ΔG is the difference between the Green function of the embedded impurity and that of the unperturbed jellium. It is written as

$$\Delta G_{v,\sigma}(r, r; E) = \frac{\sqrt{E}}{4\pi} \sum_{l=0}^{l_{\text{max}}} (2l+1) [R_{l,\sigma}(r; E) H_{l,\sigma}(r; E) - j_l(\sqrt{E}r) h_l(\sqrt{E}r)]. \quad (4)$$

$R_{l,\sigma}$ and $H_{l,\sigma}$ are, respectively, the regular and irregular solutions of angular momentum

quantum number l of the radial Schrödinger equation for the potential V_σ . Their asymptotic expansions outside the sphere of radius S are given by

$$H_{l,\sigma}(r; E) = h_l(\sqrt{E}r) \quad (5)$$

$$R_{l,\sigma}(r; E) = j_l(\sqrt{E}r) + \sqrt{E} t_{l,\sigma}(E) h_l(\sqrt{E}r) \quad (6)$$

where $h_l \equiv y_l - ij_l$. Here j_l and y_l are the spherical Bessel functions of first and second kind, respectively [16], and $t_{l,\sigma}$ is the usual scattering \mathbf{t} -matrix associated to the potential V_σ . The use of the perturbed Green function given by equation (4) allows one to consider a relatively restricted basis in the angular momentum expansions even at large distances r . Indeed, an angular momentum cut-off $l_{\max} = 3$ is usually sufficient to obtain good convergence.

Equations (2-4) are solved iteratively, using the Chebyshev iteration scheme [17]. Moreover, the use of the complex energy integration technique [18] accelerates considerably the numerical calculation.

The total neutrality of the system jellium + embedded impurity is described by Friedel's [5] sum rule

$$\Delta Z \equiv Z_{\text{imp}} - 1 = \frac{1}{\pi} \sum_{\sigma} \sum_{l=0}^{l_{\max}} (2l+1) \delta_{l,\sigma}(E_F) \quad (7)$$

where $\delta_{l,\sigma}$ are the scattering phase shifts, related to the \mathbf{t} -matrix through

$$t_{l,\sigma}(E) = -(1/\sqrt{E}) \sin \delta_{l,\sigma}(E) \exp[i\delta_{l,\sigma}(E)] \quad (8)$$

with the boundary condition $\delta_{l,\sigma}(-\infty) = 0$.

If one inserts a point charge $\Delta Z'$ into the jellium at a distance R_n from the impurity, then to first order in $\Delta Z'$ the interaction energy with the impurity is given by

$$E_{\text{int}} = \Delta Z' \Delta V_M(|R_n|). \quad (9)$$

Here ΔV_M denotes the difference between the electrostatic Madelung potential due to the single impurity in jellium and that due to a host atom treated as an impurity in the same jellium, i.e. a Cu impurity in a Cu jellium, which serves as the reference host system. Equation (9) with $\Delta Z' = -1$ has been used in the past [1-4] to calculate the interaction with a vacancy in noble metals. However, this formula is not consistent with the description of a vacancy in the jellium model and our calculations show that the results derived from it do not agree well with experiment and with the KKR calculations [10, 11]. Since by creating the vacancy the positive background charge is removed from the atomic sphere of volume Ω centred at R_n , one has to average the impurity-induced potential $\Delta V_M(|r + R_n|)$ over the atomic volume Ω . Instead of the Madelung potential change we shall use throughout the corresponding change of the electron potential energy $\Delta V_c = -\Delta V_M$. We have

$$E_{\text{int}} = \bar{\rho} \int_{\Omega} d\mathbf{r} \Delta V_c(|r + R_n|). \quad (10)$$

Equations (9) and (10) have a simple electrostatic meaning. To first order in $\Delta Z'$ the interaction energy is determined by the work done in creating the additional defect with charge $\Delta Z'$ against the Coulomb potential ΔV_c of the single impurity.

The integral over the atomic sphere in equation (10) is calculated numerically by introducing polar coordinates (r, θ, ϕ) and by using the Gauss-Legendre and the Gauss-Chebyshev integration rules for the θ - and ϕ -integrations, respectively, whereas the

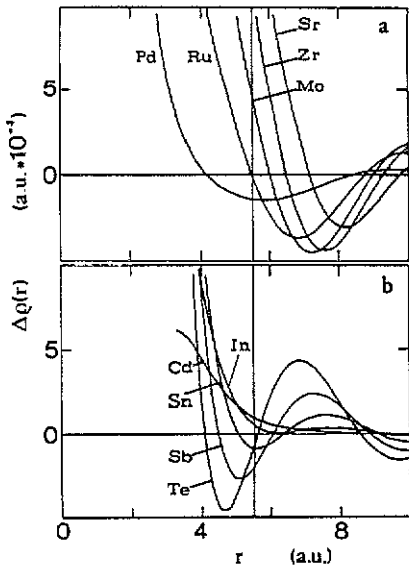


Figure 1. Electron density changes due to (a) 4d and (b) 5sp impurities in Ag: the vertical line indicates the first-neighbour distance.

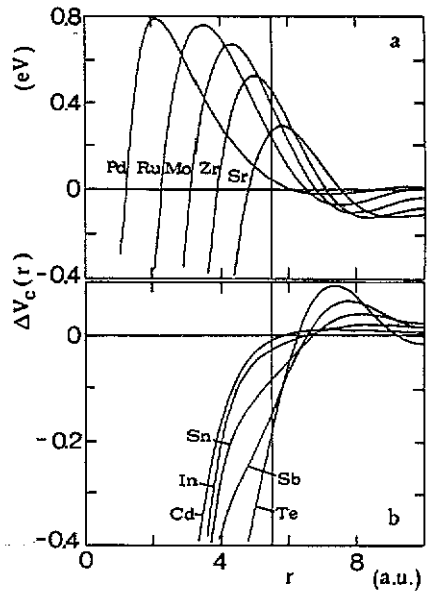


Figure 2. Changes in the electrostatic potential $\Delta V_c(r)$ due to (a) 4d and (b) 5sp impurities in Ag: the vertical line indicates the first-neighbour distance.

radial integration is performed by the repeated Simpson's rule [16]. An approximate formula for E_{int} can be derived by expanding the potential in a Taylor series around R_n . For symmetry reasons the first-order term, which is proportional to the gradient of the potential, vanishes. The second-order term which contains the second derivatives of the electrostatic potential can be evaluated using the Poisson equation relating $\Delta V_c(r)$ to the perturbed electron density $\Delta\rho(r)$. The third-order term again vanishes. Thus, up to third order the solute-vacancy interaction energy is given by

$$E_{\text{int}} \approx \Delta V_c(R_n) - (2\pi/5) r_s^2 \Delta\rho(R_n). \quad (11)$$

This equation gives interaction energies which are qualitatively correct. Quantitatively it is, however, not reliable.

3. Results and discussion

Firstly we self-consistently calculate the electronic structure of the single substitutional impurities in Cu and Ag. In order to minimize lattice relaxation effects, which are not included in the calculation, we only consider impurities from the same row of the periodic table as the host, i.e. 3d and 4sp impurities in Cu and 4d and 5sp impurities in Ag. An angular momentum cut-off $l_{\text{max}} = 3$ and a range of the perturbing potential $S = 10$ au are sufficient to obtain adequate convergence in all cases examined. Charge neutrality within the sphere of radius S is never violated by more than a few hundredths of an electron, and Friedel's sum rule is satisfied to within a few per cent.

Figures 1(a) and 1(b) show the changes in the electron densities due to 4d and 5sp impurities, respectively, in Ag. The 3d and 4sp impurities, respectively, in Cu exhibit a

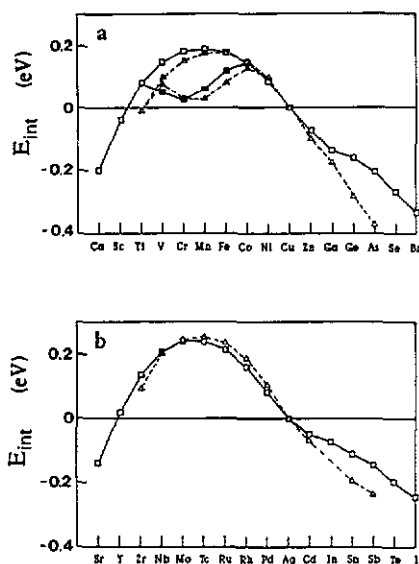


Figure 3. Interaction energies between an impurity and a vacancy at first-neighbour sites in (a) Cu and (b) Ag as calculated by the jellium model (—) and the results obtained by the KKR Green function method (---): \blacktriangle , \blacksquare , spin-polarized solutions.

similar behaviour [11]. Outside the impurity atomic sphere the perturbed density $\Delta\rho(r)$ is an oscillatory decreasing function. For a Pd impurity in Ag the nearest-neighbour distance $R_1 = 5.50 \text{ au}$ lies in a shallow valley of $\Delta\rho$. This valley deepens and shifts outwards for impurities in the sequence Pd to Sr. Thus, for Ru we have $\Delta\rho(R_1) \approx 0$, whereas for the early 4d impurities there is a positive density change at the nearest-neighbour distance which strongly increases with increasing valence difference. In the case of 5sp impurities in Ag we observe for Cd and In a shallow minimum near R_1 which deepens and shifts inwards for the higher-valency impurities. From these results it is clear that the Thomas-Fermi approximation fails to describe the charge density changes, since it yields a positive and exponentially decreasing charge density for the sp impurities. Thus, the approach of Lazarus [1] and Le Claire [2] for the interaction energies is unjustified and the reasonably good agreement obtained with experiment is accidental.

In figures 2(a) and 2(b) we show the changes in the electrostatic potentials $\Delta V_c(r)$ induced by 4d and 5sp impurities, respectively, in Ag. The 3d and the 4sp impurities, respectively, in Cu exhibit a similar behaviour [11]. We observe that the perturbation of the electrostatic potential tends to zero by oscillating away from the impurity. For the 4d impurities the oscillations of ΔV_c start below R_1 and the first maximum is raised up and shifts inwards in the sequence Sr to Pd. The value of ΔV_c at the nearest-neighbour distance is always positive and largest for Zr, where the maximum occurs very close to R_1 . On the contrary, for the 5sp impurities the Coulomb potential is more attractive than for the reference system (an Ag impurity in an Ag jellium) up to R_1 . Thus, $\Delta V_c(R_1)$ is always negative in the case of 5sp impurities in Ag and roughly scales with the valence difference (figure 2(b)).

Figures 3(a) and 3(b) show the interaction energies between an impurity and a vacancy at first-neighbour sites in Cu and Ag hosts, respectively, calculated from equation (10). Negative energies mean attraction and positive energies repulsion of the two defects. In the same figure we also report the results obtained by the KKR Green function method [10, 11]. It is seen that both approaches give quite similar trends. The

deviations essentially arise from the host band structure and especially the host d band which cannot be taken into account in the jellium model.

For the sp impurities, one obtains an attraction roughly proportional to the valence difference ΔZ . This conclusion could be reached very simply by considering the vacancy as the strong defect and the sp impurity as a perturbation. An early sp impurity with, for example, $\Delta Z' = +1, +2$ can be obtained by firstly removing the positive background charge density from the sphere (R_n, r_s) and then by uniformly spreading the ionic charge of the impurity within this sphere. Thus, in analogy to equation (10), one obtains that E_{int} is proportional to $\Delta Z'$. The proportionality constant is equal to minus the average of the self-consistent electrostatic potential due to a single vacancy over the sphere (R_n, r_s). For a first-neighbour position in Cu (Ag) we find this proportionality constant to be -0.07 eV (-0.03 eV). These values are in good agreement with the results obtained by considering the all-electron sp impurity as the strong defect and the vacancy as perturbation (see figure (3)).

However, contrary to the KKR results, where the interaction energy varies more or less linearly as a function of ΔZ for almost all the sp impurities, we find that, except for impurities with $\Delta Z = \pm 1$, there are strong deviations from this linear behaviour. The almost linear behaviour found in the KKR calculations for larger ΔZ -values is very probably due to p impurity-d host hybridization, which is very appreciable for the multivalent impurities. Note that the deviations from the jellium results are larger in Cu than in Ag, because the d band of Ag is lower in energy and correspondingly the d electrons are more strongly localized, so that the p-d hybridization is weaker. Therefore, the jellium results are somewhat more appropriate for Ag than for Cu.

For non-magnetic transition-metal impurities the interaction is repulsive and shows a parabolic behaviour with a maximum in the middle of the series. In the presence of a vacancy the virtual bound state of a nearby impurity becomes narrower owing to the loss of hybridization which then explains the loss of bonding and the repulsion from the vacancy. The parabolic behaviour of the interaction energy is a band-filling effect and is qualitatively very similar to that of the cohesive energies of elemental transition metals as explained by Friedel [19]. For the early d impurities, only the lower bonding parts of the virtual bound state are occupied whereas, for the later d impurities, also the higher antibonding states are filled. If we allow for spin polarization, the calculation for V, Cr, Mn and Fe impurities in Cu converges to a magnetic solution. The presence of a vacancy on a neighbouring site reduces the hybridization of the 3d impurity orbitals with the host states and this leads to an enhancement of the local moment. The corresponding gain of exchange energy, which becomes larger as the impurity moment increases, partly cancels the loss of bonding close to the vacancy, thus explaining the reduced repulsion of the 3d impurities in Cu in the spin-polarized calculation.

This effect can be also explained in terms of the change in the electrostatic potential. Indeed, as shown in figure 4, the repulsive potential $\Delta V_c(r)$ for V, Cr, Mn and Fe impurities in Cu is strongly reduced near the first-neighbour site if we take spin polarization into account.

As can be seen from figure 3, our calculation yields a somewhat larger 'magnetic' reduction in the interaction energy for V and Cr impurities than the KKR results, whereas for Mn and Fe impurities this reduction is somewhat underestimated. This can be explained as follows. In a realistic electronic structure calculation the hybridization between the low-lying host 3d and the impurity 3d states repels the impurity d states to higher energies [20]. As a result, for an impurity with a less than half-filled d shell the local density of states at E_F decreases. This leads finally to a smaller magnetic moment

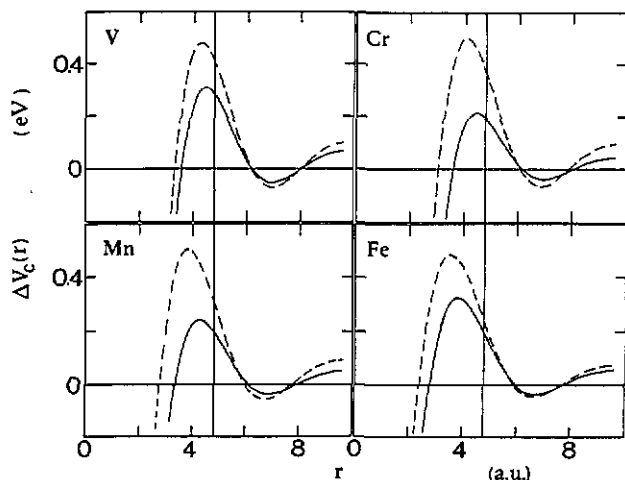


Figure 4. Changes in the electrostatic potential $\Delta V_e(r)$ due to magnetic 3d impurities in Cu: the vertical line indicates the first-neighbour distance; —, spin-polarized calculation; ---, non-spin-polarized calculation.

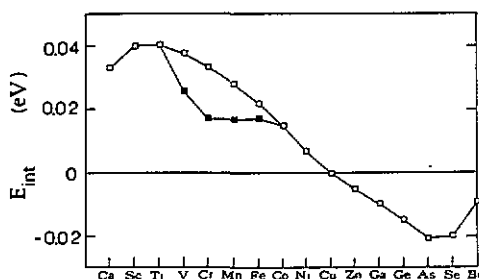


Figure 5. Interaction energies between an impurity and a vacancy at second-neighbour sites in Cu: ■, spin-polarized solutions.

and consequently to a smaller reduction in the interaction energy compared with the results of a jellium calculation, where the low-lying host 3d states are neglected. Similarly in our calculation, for an impurity with a more than half-filled d shell, the lack of host d-impurity d hybridization leads to an underestimation both of the impurity moment and of the reduction in the solute-vacancy interaction.

Comparison with experiments is rather difficult since very few reliable data on the vacancy-solute interaction exist. However, a detailed comparison between KKR results and the available experimental information has been reported by Klemradt *et al* [11]. Thus, we shall not attempt here a discussion of our results in connection with the experiment, since they agree reasonably well with those obtained by the KKR method. Despite the difficulties in estimating solute-vacancy interaction energies from various measurements there is overall agreement between theoretical results and experimental data deduced from diffusion, positron annihilation and perturbed angular correlation experiments.

When vacancies occupy sites further away than the first-neighbour sites of the impurity, we find that the interaction becomes very small, in agreement with the KKR results [10, 11]. In figure 5 we show the solute-vacancy interaction energies for second-neighbour positions in a Cu matrix. The curve obtained is similar to that in figure 3

corresponding to first-neighbour interaction, but it is typically ten times smaller in scale and shifted towards the first elements of the periodic table row. We find also that 4sp impurities are attracted by the vacancy and that the solute–vacancy interaction energy for early 4sp impurities is proportional to the valence difference ΔZ as it is in the case where the vacancy is first neighbour to the impurity. The proportionality constant is found to be -0.005 eV (see figure 5). If we treat the vacancy as the strong defect and the sp impurity as the perturbation, we calculate this proportionality constant to be -0.003 eV.

The overall agreement between our results and those of KKR total energy calculations shows that the first-order approximation (10) for the interaction energy is sufficiently accurate.

In the approach of Blandin and co-workers [3] the vacancy was created by superimposing a point charge $\Delta Z' = -1$ on the jellium positive background at point R_n . This leads to an interaction energy equal to $\Delta V_c(R_n)$ (see equation (9)). However, we demonstrate here that averaging the potential over a neighbouring atomic sphere according to equation (10) is quite important. For instance, for the 3d impurities in Cu, $\Delta V_c(R_1)$ has its maximum for Ti (0.41 eV) whereas E_{int} is maximal for Mn (0.19 eV) in the non-spin-polarized calculation and has a value of 0.08 eV for Ti. Similarly, for the 4d impurities in Ag, $\Delta V_c(R_1)$ has its maximum value for Zr (0.46 eV) whereas E_{int} is maximum for Mo (0.24 eV) and has a value of 0.13 eV for Zr. These differences can be explained by using the approximate formula (11) for the interaction energy. Indeed, owing to the strong charge perturbations $\Delta\rho(R_1)$ for the early transition-metal impurities (see figure 1(a)), $\Delta V_c(r)$ deviates for smaller distances considerably from its value at R_1 (see figure 2(a)). On the contrary, for the sp impurities the corrections to the point charge model are not very important, since the corresponding perturbed charge densities $\Delta\rho(R_1)$ are much smaller. Moreover, Blandin and co-workers [3] derived $\Delta V_c(R_1)$ from the asymptotic form of charge-density oscillations [5] using a rough estimate for the impurity phase shifts in which they supposed that the impurity is screened only by d electrons. This derivation of $\Delta V_c(R_1)$ is not sufficiently accurate. We have shown that the asymptotic form of the Friedel oscillations is not valid at the first-neighbour distance and the neglect of sp screening leads to errors as large as 30% in the d-phase shifts for 3d impurities in Cu [21].

4. Conclusion

We performed self-consistent calculations within the framework of the local-spin-density-functional theory for the interaction energies of vacancies with 3d and 4sp impurities in Cu as well as with 4d and 5sp impurities in Ag. The calculations are based on the jellium model and first-order perturbation theory. The results obtained are in agreement with those calculated by first-principles methods and show the observed experimental trends. This model provides a very simple explanation of the interaction in terms of the electrostatic potential of the single impurity. We have also shown that a consistent and reliable calculation of this potential is required. The close agreement with the experiment found in earlier calculations [1–4] is more or less accidental and due to error cancellations of the different unreliable approximations involved.

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