Interaction Energies of Impurities in Cu and Ni

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We present systematic local-density-functional calculations for the interaction energies of $3d$ and $4sp$ impurities (Sc–Br) with vacancies in Cu and Ni crystals. We apply the Kohn-Korringa-Rostoker Green's-function method and evaluate the full anisotropic charge density. The interaction energies are obtained by total-energy calculations and by a newly derived formula based on the Hellmann-Feynman theorem. Both methods agree very well and confirm the experimentally known trends.

The knowledge of the interaction energies of point defects in solids is indispensable to the understanding of many basic physical processes, such as diffusion, short-range order, segregation, ordering, etc. As experience has shown, it is very difficult to obtain reliable information on the interactions, both theoretically and experimentally. Previous calculations based either on the jellium model,[1,2] on pseudopotentials combined with second-order perturbation theory,[3,4] or on the tight-binding method[5] are only of restricted use because of the inherent limitations of these methods. The pioneering work in this field is due to Deplante and Blandin,[1] who performed jellium-type calculations for interactions between vacancies and $3d$ and $4sp$ impurities in Cu and obtained qualitatively reasonable results. Gupta[2] tried to improve these calculations, but with limited success. Pseudopotentials in second-order perturbation theory can only be used for simple metals. The application to impurities with nuclear charges $\Delta Z = \pm 1$ already seems to be problematic,[4] and even more so the treatment of vacancies.[6] While the tight-binding calculations[5] possible for transition metals contain a lot of physics, they are notoriously plagued by unknown parameters. There is clearly a strong need for realistic *ab initio* calculations, which should have the same accuracy and predictability as present-day, state-of-the-art results for ideal crystals. To our knowledge such calculations have not been performed until now. It is our aim in the present Letter to describe the methods for accurate *ab initio* calculations of interaction energies and to demonstrate their success for particular examples. Here we choose as host crystals Cu (a "simple" noble metal) and Ni (a ferromagnetic transition metal) and consider the interaction between an impurity and a vacancy on nearest-neighbor sites.

We apply density-functional theory in the local-density approximation of von Barth and Hedin[7] with the parameters as given by Moruzzi, Janak, and Williams.[8] The calculations are based on the Kohn-Korringa-Rostoker (KKR) Green's-function method for impurity calculations[9] and on a recently developed accurate total-energy formalism.[10] In the KKR Green's-function method the Green's function of the system is expanded in

each cell into radial eigenfunctions of the local potential, assumed to be spherically symmetric within Wigner-Seitz spheres. All the multiple-scattering information is contained in the structural Green's-function coefficients $G_{LL'}^{nn'}(E)$, which are related to the ones $\bar{G}_{LL'}^{nn'}(E)$ of the ideal crystal by a Dyson equation,[9]

$$G_{LL'}^{nn'}(E) = \bar{G}_{LL'}^{nn'}(E)$$
$$+ \sum_{L'',n''} \bar{G}_{LL''}^{nn''}(E)\Delta t_{l''}^{n''} G_{L''L'}^{n''n'}(E). \tag{1}$$

Here $\Delta t_{l}^{n} = t_{l}^{n} - \bar{t}_{l}^{n}$ are the changes of the t matrices in the vicinity of the defect. The solution of this Dyson equation involves the inversion of matrices, the rank of which is determined by the number of perturbed potentials and the number of angular momenta taken into account.

In our calculations we consider two point defects on nearest-neighbor sites and allow the potentials of all host atoms to be perturbed which are nearest neighbors to at least one of the defects. These are twenty perturbed potentials in total, which are calculated self-consistently. Angular momenta up to $l = 3$ are taken into account. As shown in Ref. 10 both approximations are sufficient to obtain reliable total energies. The single-particle energies are calculated by Lloyd's formula, thus including the contributions over all space and for all angular momenta. The double-counting contributions for both the Coulomb and the exchange energies are calculated using the full anisotropic charge density in each cell. In the present calculations we approximate the integrals over Wigner-Seitz cells by integrals over atomic spheres. This approximation leads to sufficiently accurate interaction energies as more refined calculations with integrations over the exact faceted Wigner-Seitz cell show.[11]

The interaction energy between point defects A and B is calculated as the total-energy difference between three different defect configurations, the AB complex, the single A defect, and the single B defect, which are all calculated using potential perturbations over 20 atoms and the same approximations. If $\Delta E_{(AB)}$ is the excess energy (with respect to the energy of the ideal crystal) for the AB complex, and $\Delta E_{(A)}$ and $\Delta E_{(B)}$ the corresponding ex-

cess energies for the single A and B defects, then the interaction energy is given by $\Delta E = \Delta E_{(AB)} - \Delta E_{(A)} - \Delta E_{(B)}$. In principle, ΔE also contains contributions from lattice relaxations. To avoid this complication we restrict ourselves to systems for which lattice relaxations are not of major importance, i.e., $3d$ and $4sp$ impurities in Cu and Ni. We have chosen these hosts since Cu is normally considered as a simple metal and a kind of prototype for electronic-structure calculations, whereas Ni is a transition metal and, moreover, ferromagnetic. Single impurities show a very different behavior in these hosts; e.g., $3d$ impurities have an endothermic solubility in Cu, but an exothermic one in Ni.[10]

As a central result of our work Fig. 1 shows the calculated interaction energies between a vacancy and an impurity of the $3d$ and $4sp$ series. Positive energies mean repulsion of the two defects; negative energies, attraction. For the sp impurities in Cu and in Ni one obtains a strong attraction being roughly proportional to the valence difference ΔZ. While such a proportionality is expected in Cu from pseudopotential theory (see below) the fact that it also holds in Ni and in both cases up to large valence differences $\Delta Z = 5$ to 6 is very surprising. We will come back to this later.

For the transition-metal impurities the interaction with the vacancy is repulsive and shows a more complicated behavior. The dip in the middle of the $3d$ series arises from magnetism. A calculation without spin polarization for Cu (dotted line) shows a very smooth repulsive behavior throughout the whole $3d$ series. The inverted parabolic curve is quite similar to the trends of cohesion or surface energies of transition metals: Here it is the bonding between the $3d$ electrons of the impurity and the $4sp$ states of Cu which is partially lost at the vacancy. The large magnetic effects arise because the impurity moments are enhanced near a vacancy as a consequence of the reduced coordination number. The same

effect is well known to enhance magnetism at surfaces. The gain of exchange energy 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.

The comparison with experiments is rather difficult since very few reliable data about the vacancy-solute interaction exist.[12] The best studied case is the interaction of Ge impurities with vacancies in Cu. From positron measurements Doyama et al.[13] obtain -0.27 ± 0.10 eV, whereas Triftshäuser and Jank[14] give -0.23 ± 0.10 eV. Both values compare well with our calculated value of -0.25 eV for the interaction energy of a Ge atom in Cu. Solute-diffusion data can also give valuable information about the binding energies. The general trends found in diffusion experiments in Cu (see, e.g., Fig. 1 in Ref. 15) are in agreement with the trends we obtain, i.e., a repulsion for the $3d$ impurities and an attraction roughly linear to ΔZ for sp ones. A detailed analysis of the CuGe system[16] gives a binding energy of -0.18 ± 0.08 eV, whereas for NiGe,[17] a binding energy of -0.20 ± 0.06 eV is obtained (compared to our value of -0.29 eV). Note that the experimental values are free energies which also contain some entropy contributions. The close agreement between the calculated and experimental values suggests that these are small.

Since the calculated interaction energies represent the changes of the vacancy formation energy due to a neighboring impurity, one would expect a correlation with the vacancy formation energy of the corresponding metals. This is, however, complicated due to the different lattice constants and crystal structures of these metals. Nevertheless, the vacancy formation energies of Zn (0.54 eV) and Al (0.66 eV) are indeed appreciably smaller than the one of Cu (1.28 eV) whereas those of the transition metals are in general larger (Ni, 1.79 eV; Fe, 1.8 eV). Another correlation might be even more important. By considering the vacancy as a small internal surface, one would expect the same, but enlarged trends for the binding energies at real surfaces. Thus our vacancy binding energies should predict the trends of surface segregation in Cu and Ni.

Total energies are in general difficult to interpret especially since they are the differences of very large partial energies. Because of their small size this is a serious problem for the interaction energies. In the following we derive a new and exact formula for the Hellmann-Feynman theorem and give a direct relation of the interaction energies to the screening charge densities of the impurities. For this we consider the nuclear charge Z_A of the defect A as an external continuous parameter. The derivative dE/dZ_A of the total energy is given by
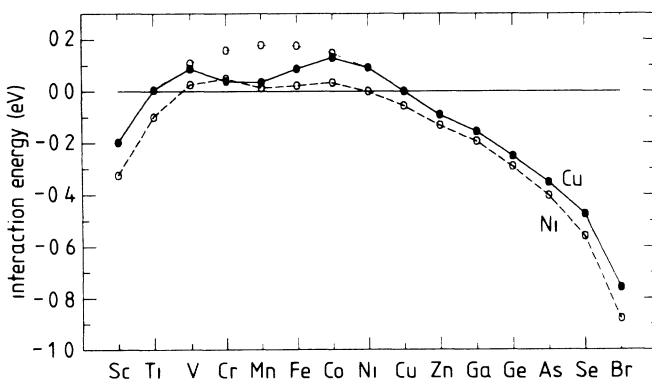

FIG. 1. Interaction energy of the impurity-vacancy complex on nearest-neighbor sites in Cu (solid line) and Ni (dashed line). The dotted line refers to non-spin-polarized calculations for $3d$ impurities in Cu. Positive energies mean repulsion; negative ones, attraction.

$$\frac{dE}{dZ_A} = \frac{\partial E}{\partial Z_A}\bigg|_{n(\mathbf{r})} + \int d\mathbf{r}\, \frac{\delta E}{\delta n(\mathbf{r})} \frac{dn(\mathbf{r})}{dZ_A}$$

$$= V_M(\mathbf{R}_A) + E_F. \qquad (2)$$

The first term, the derivative with respect to the explicit dependence of the functional $E\{n(\mathbf{r})\}$ on the nuclear charge Z_A, yields the Madelung potential $V_M(\mathbf{R}_A)$ at the nuclear position $\mathbf{R}_A$ due to all other nuclei and all electrons:

$$V_M(\mathbf{R}_A) = \sum_{n \neq A} \frac{Z_n}{|\mathbf{R}_A - \mathbf{R}_n|} - \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} . \quad (3)$$

The second term in (2) arising from the implicit dependence on Z_A yields the Fermi energy E_F because the considered states are always neutral and $\delta E/\delta n(\mathbf{r}) = E_F$. The result (2) allows a simple classical interpretation: $V_M(\mathbf{R}_A)dZ_A$ is the energy gained by increasing the nuclear charge against the Coulomb potential of all other charges, while $E_F dZ_A$ is the energy gained by adding dZ_A electrons to the system to achieve neutrality. By integrating (2) from the host value Z_H to the true value Z_A of the impurity we obtain the energy difference $E(Z_A) - E(Z_H)$. In order to obtain a formula for the interaction energy ΔE between defect A and B, we "create" the defect A once with defect B on a nearest-neighbor site and once without defect B, which is equivalent to defect B being infinitely far away. We obtain for the interaction energy

$$\Delta E = \int_{Z_H}^{Z_A} dZ_A' \{V_M(\mathbf{R}_A; Z_A', Z_B) - V_M(\mathbf{R}_A; Z_A', Z_H)\} , \quad (4)$$

where $V_M(\mathbf{R}_A; Z_A', Z_B)$ is the Madelung potential at the nuclear site $\mathbf{R}_A$ of defect A with nuclear charge Z_A', if the second defect has the charge Z_B. Since the Madelung potential contains the charge density $n(\mathbf{r})$ as the only nontrivial information, Eqs. (3) and (4) give a very direct and exact relation between the interaction energy and the charge density. Contrary to the total-energy expression the charge density for all intermediate nuclear states between Z_H and Z_A is needed. Moreover, errors in the charge density enter to linear order as compared to second order in the total-energy expression (due to its extremal properties). Despite this, considerable advantages arise from (4) due to its simplicity and its direct relation to the charge density, as we demonstrate in the following.

Figure 2 shows a comparison between the solute-vacancy interactions in Cu as calculated from the total energy and from expression (4) based on the Hellmann-Feyman theorem. The Z_A' integration has been performed by the trapezoidal rule with a $\Delta Z_A'$ spacing of $\Delta Z_A' = 1$, so that only integer nuclear charge states are used. Evidently all the calculated trends are already obtained in this approximation. Even the dip in the middle of the $3d$ series, caused by the enhanced local moments of the $3d$ impurities close to the vacancy, is well reproduced. This is an especially remarkable fact since in Eq. (4) only the charge density explicitly enters in the form of the Coulomb potential, but not the magnetization density or the exchange potential. The close agreement between both curves is also an important check for the ac-
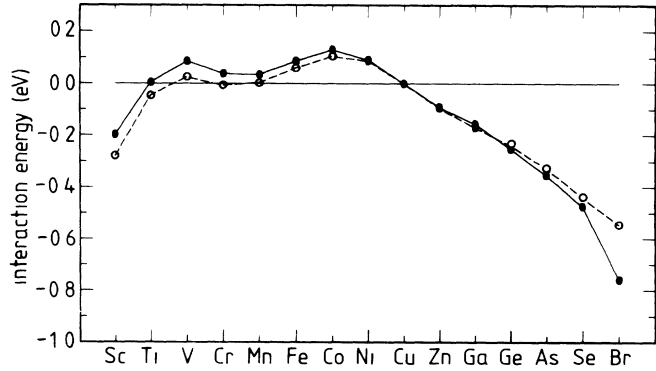

FIG. 2. Interaction energies of impurities with a vacancy in Cu, as calculated from the total energies (solid line) and from the Hellmann-Feynman expression (2) (dashed line).

curacy of the calculation. The agreement becomes even somewhat better if half-integer nuclear charges are used for the Z_A' integration in combination with Simpson's rule. Equation (4) and Fig. 2 clearly demonstrate that the total energy can be directly determined from the charge density provided this is known with sufficient accuracy.

If the defect A represents a weak perturbation, in (4) the Z_A' dependence of the potentials may be neglected, yielding the formula of Deplante and Blandin:[1]

$$\Delta E \cong \Delta Z_A [V_M(\mathbf{R}_A; Z_B) - V_M(\mathbf{R}_A; Z_H)]$$

$$= \Delta Z_A \Delta V_M^B(\mathbf{R}_A) , \quad (5)$$

where $\Delta V_M^B(\mathbf{R}_A)$ is the change of the Madelung potential of a host atom at site $\mathbf{R}_A$, if the defect B alone is present in the crystal. Since no assumption is made about the strength of defect B, we, e.g., might identify B with a vacancy. As weak defect A we consider an sp impurity for which the interaction energy scales with the excess charge ΔZ_A, both in Cu and Ni (see Fig. 1). Indeed, the slopes of the ΔE curves in Fig. 1 agree reasonably well with the calculated potentials ΔV_M^B for single vacancies. Equation (5) represents a very convenient way to calculate the interaction energy since only the screened Coulomb potential of a single defect must be calculated. As an application we calculate how the interaction of $4sp$ impurities with a vacancy in Cu, Ag, and Ni (Fig. 3) depends on the distance between the two defects. The interaction is dominated by the strong attraction on nearest-neighbor sites and is rather weak at larger distances, especially for Cu, and of oscillatory character. Analogously the agglomeration of a third defect to an impurity-vacancy complex could be studied by just calculating ΔV_M for the pair complex.

In summary, we have presented accurate local-density-functional calculations for the interaction energies of impurities with vacancies in Cu and ferromagnetic Ni. For both hosts we obtain quite similar trends: $3d$
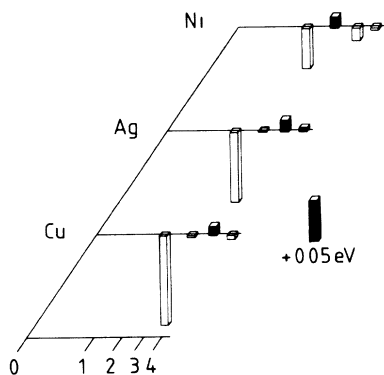
FIG. 3. Distance dependence of the Madelung potential $\Delta V_M^B(\mathbf{R}_A)$ of a single vacancy in Cu and Ni for the first four shells. For sp impurities the interaction energy is obtained according to Eq. (4) by multiplying with the valence difference ΔZ_A. Negative energies are marked as open columns; positive as full ones.

impurities are repelled from the vacancy, strongly in Cu and somewhat more weakly in Ni, whereas $4sp$ impurities are strongly bound by the vacancy with energies scaling with the valence difference ΔZ. We believe that these results are generally valid for all late transition metals as hosts. By applying the Hellmann-Feynman theorem with the nuclear charge of the impurity as an external variable we derive a new and exact formula for the interaction energy which focuses on the electrostatic origin of the interaction. We demonstrate that the simplicity of this formula has considerable advantages compared to the usual total-energy expression.

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