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Theory of vacancies near a bimetallic interface

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The theory of vacancies near a bimetallic interface is developed within a tight-binding model. It is shown that the local density of states is significantly influenced only in the immediate vicinity of the vacancy, and that the vacancy-formation energy is an oscillatory function of the distance of the vacancy from the interface. For the specific interface considered the vacancies tend to be attracted towards the interface. In the extreme case a vacancy can gain more than 10 percent of its formation energy by migrating from the bulk to the interface region. When two vacancies are present in the system they interact due to the polarization of the medium. This interaction is shown to have an oscillatory dependence on the intervacancy separation. The nearest-neighbor interaction of the interface considered is found to be attractive with an energy which is about 1/3 of the vacancy-formation energy.

I. INTRODUCTION

The quantum-mechanical theory of solid-solid interfaces is a relatively new branch of surface physics. The electronic structure of such interfaces has been recently studied by several authors. The interest in this kind of problem stems from both theoretical and practical origins. One can say that the technological need for a better understanding of metal-semiconductor and semiconductor-semiconductor junctions, bimetallic adhesion, grain boundaries, friction, and similar problems served as a catalyst for the various studies in this area.

The electronic properties of a bimetallic interface formed by two simple metals were analyzed by Bennett and Duke,[1] Ferrante and Smith,[2] Rouhani and Schuttler,[3] and Mehrotra, Pant, and Das.[4] In these theories the two metals were treated within the jellium model, using the density-functional formalism of Hohenberg, Kohn, and Sham.[5]

The electronic properties of bimetallic and metal-semiconductor interfaces were discussed recently, using tight-binding models, by Davison and Cheng,[6] Allan, Lannoo, and Dobrzynski,[7] Muscat, Lannoo, and Allan,[8] Yaniv,[9] and Lowy and Madhukar.[10]

All the models developed thus far deal with an ideal, coherent interface which is formed by matching two semi-infinite solids having the same translational symmetry parallel to the interface. Such systems obey a two-dimensional Bloch theorem, and the crystal momentum parallel to the interface is a good quantum number. This relatively high degree of symmetry was taken advantage of by the above-mentioned investigators in order to simplify the solution of the interface problem. However, real interfaces certainly do contain various types of defects near the interface. The presence of such defects lowers the symmetry of the system, and even the two-dimensional Bloch theorem is not applicable. Therefore, the crystal momentum parallel to the interface cannot be used any more as a good, conserved, quantum number.

One of the simplest possible defects which destroys the translational symmetry parallel to the interface is the presence of a vacancy, i.e., one of the atoms is missing from its original lattice site. The present work is devoted to the study of the electronic structure of vacancies close to a bimetallic interface. As our starting point we adopt the tight-binding coherent interface studied by us earlier.[9] Similar models were used extensively in the literature to study the electronic properties of transition metals. The contribution to various quantities, such as the bulk cohesive energy, the bulk vacancy-formation energy, and the surface energy, evaluated within a one-electron single tight-binding band, give quite a good qualitative agreement with experiment. Thus, corrections due to electron-electron interaction, changes in the elastic energy of the solid near the vacancy, and other fine effects are neglected also in the present work.

The one-band tight-binding model, whose details are outlined in Sec. II, can be viewed as a crude description of an interface formed between two transition metals. The local density of states in the vicinity of a vacancy close to the interface is determined in Sec. III by using a Green's-function perturbation technique. Also evaluated in Sec. III is the vacancy-formation energy, whose dependence on the distance from the interface is discussed. Section IV analyzes the vacancy-vacancy interaction mediated by the polarization of the medium.

II. THE MODEL

The electronic structure of a coherent, tight-binding, bimetallic interface was studied by us recently.[9] This work will be used in the following as a starting point for the investigation of the properties of vacancies formed close to such an interface. For the sake of simplicity, the present article deals with a (100) interface formed between two simple cubic metals. Each metal is described by a single-band tight-binding Hamiltonian. We shall treat explicitly the case where the two metals are described by the same tight-binding parameters but have different Fermi energies. The hopping integral between the two semi-infinite metals is taken to be equal to the bulk value. We also assume that the Hamiltonian has a tenfold degeneracy. This simple model can serve as a crude model describing the electronic properties of a (100) interface formed between two transition metals belonging to the same series, and will be referred to as such in the following. The interface is taken to be in the xy plane, and the two metals forming the junction, metal a and metal b, to occupy the upper and the lower semi-infinite half spaces, respectively.

The difference in the Fermi energies of the two metals leads to the creation of a dipole layer at the interface, which in turn aligns the Fermi levels. The magnitude of the dipole barrier is $2\Delta V$, where

$$\Delta V = \tfrac{1}{2}(E_F^a - E_F^b) \equiv \tfrac{1}{2}\Delta E_F , \tag{2.1}$$

E_F^a and E_F^b being the Fermi energies of metal a and b, respectively. The common Fermi level, after the junction is created, is given by

$$E_F = E_F^a - \Delta V = E_F^b + \Delta V = \tfrac{1}{2}(E_F^a + E_F^b) . \tag{2.2}$$

The Hamiltonian of the coherent interface, in the Wannier representation, is taken to be

$$H^0 = \sum_{\vec{m},\vec{n}} t_{\vec{m},\vec{n}}\, c_{\vec{m}}^\dagger c_{\vec{n}} , \tag{2.3}$$

where $c_{\vec{m}}^\dagger$ and $c_{\vec{m}}$ are the creation and the destruction operators of a Wannier orbital at the lattice site $\vec{m}$. The matrix elements $t_{\vec{m},\vec{n}}$ are

$$t_{\vec{m},\vec{n}} = \begin{cases} -\Delta V & \text{if } \vec{m} = \vec{n} \text{ and } \vec{m} \text{ is an } a \text{ site} , \\ +\Delta V & \text{if } \vec{m} = \vec{n} \text{ and } \vec{m} \text{ is a } b \text{ site} , \\ E_1 & \text{if } \vec{m} \text{ and } \vec{n} \text{ are nearest neighbors} , \\ 0 & \text{otherwise} . \end{cases} \tag{2.4}$$

In writing the above expression we assumed that the energy is measured relative to the center of the bands. Also, E_1 is the transfer integral, or the nearest-neighbor hopping amplitude.

The coherent interface Hamiltonian (2.3) has a translational symmetry parallel to the interface. Because of this symmetry, the corresponding eigenfunctions can be chosen to satisfy a two-dimensional Block theorem, and the crystal momentum parallel to the interface, $\vec{k}_\parallel$, is a good quantum number. Owing to this symmetry, it is convenient to describe the coherent interface in a mixed Bloch-Wannier representation[11]

$$|\vec{k}_\parallel , n\rangle = N_\parallel^{-1/2} \sum_{\vec{n}_\parallel} |\vec{n}\rangle e^{i\vec{k}_\parallel \cdot \vec{n}_\parallel} , \tag{2.5}$$

where $|\vec{n}\rangle$ is a Wannier orbital localized at the lattice site $\vec{n}$, $N_\parallel$ is the number of atoms in the interface plane, $\vec{n}_\parallel$ is a lattice translation parallel to the interface which equals to the transverse component of $\vec{n}$, whereas n is the corresponding perpendicular component. The basis functions (2.5) are Wannier-type perpendicular to the interface, and Bloch-type parallel to it. Thus $|\vec{k}_\parallel , n\rangle$ is localized around the nth plane parallel to the interface, and has a crystal momentum $\vec{k}_\parallel$ in the same plane. We note that the planes $n \geqslant 0$ are occupied by a-type atoms, whereas b-type atoms occupy the $n \leqslant -1$ planes.

The diagonal matrix elements of the coherent interface Green's function, in the Bloch-Wannier representation, were determined analytically in Ref. 9. The general matrix elements of this Green's function, $G^0(m,n;\vec{k}_\parallel)$, can also be determined in an analogous way. For the model under consideration these matrix elements, for a (100) interface, are given by

$$G^0(m,n) = \frac{i}{\mu_a}\left(\frac{\omega_a + i\mu_a}{2E_1}\right)^{|m-n|} + \frac{1}{\mu_a + i\omega_a}\left(\frac{\omega_a + i\mu_a}{2E_1}\right)^{m+n}\left(\frac{i\mu_a + \omega_a}{\mu_a} - \frac{8E_1^2 i}{4E_1^2 + (\mu_a + i\omega_a)(\mu_b + i\omega_b)}\right) , \tag{2.6a}$$

for $m, n \geqslant 0$ and by

$$G^0(m,n) = \frac{-4E_1}{4E_1^2 + (\mu_a + i\omega_a)(\mu_b + i\omega_b)}\left(\frac{\omega_a + i\mu_a}{2E_1}\right)^{m}\left(\frac{\omega_b + i\mu_b}{2E_1}\right)^{|n+1|} \tag{2.6b}$$

for $m \geqslant 0$ and $n \leqslant -1$. In these equations

$$\omega_a = E + \Delta V - 2E_1[\cos(k_x a) + \cos(k_y a)] , \tag{2.7a}$$

$$\omega_b = E - \Delta V - 2E_1[\cos(k_x a) + \cos(k_y a)] , \tag{2.7b}$$

and

$$\mu = \begin{cases} (4E_1^2 - \omega^2)^{1/2} & \text{for } \omega^2 \leqslant 4E_1^2 \\ i\,\mathrm{sgn}(\omega)(\omega^2 - 4E_1^2)^{1/2} & \text{for } \omega^2 > 4E_1^2 . \end{cases} \tag{2.8}$$

When a localized vacancy is created, the translational symmetry parallel to the interface does not exist any more. Under these circumstances, the Bloch-Wannier representation (2.5) loses its convenience, and one has to turn to the Wannier, site-localized, basis functions. It follows from the transformation law (2.5) that the Wannier representation of the Green's function is related to its Bloch-Wannier representation by

$$G^0(\vec{m},\vec{n})=(2\pi)^{-2}\int d\vec{k}_{\parallel}G^0(m,n;\vec{k}_{\parallel})e^{i\vec{k}_{\parallel}\cdot(\vec{m}_{\parallel}-\vec{n}_{\parallel})}\;, \tag{2.9}$$

where the $\vec{k}_{\parallel}$ integration goes over the two-dimensional Brillouin zone, defined by the coherent interface symmetry.

In order to create a vacancy at a given site $\vec{n}$, we have to break the bonds connecting the atom located at that site with its nearest neighbors. An alternative method is to apply a very strong repulsive potential on the site under consideration.[12] The application of such a potential ensures that this site will be unoccupied. The second approach is simpler from the computational point of view, and will be adopted in the following. Therefore, the perturbation potential, associated with the creation of a vacancy at site $\vec{n}$, is taken to be

$$V_{\vec{n}}=\lim_{V_0\to\infty}V_0c^{\dagger}_{\vec{n}}c_{\vec{n}}\,. \tag{2.10}$$

This perturbation is applied in the following section in order to determine the properties of a vacancy near a bimetallic interface. In what follows we shall always assume that we are dealing with vacancies formed in metal a.

III. ELECTRONIC STRUCTURE AND THE FORMATION ENERGY OF A VACANCY

In order to investigate the electronic structure in the vicinity of a vacancy we shall use the Green's-function method. Starting from the coherent interface Green's function we generate the Green's function in the presence of a vacancy by applying the perturbation (2.10) via Dyson's equation

$$G=G^0+G^0VG\,, \tag{3.1}$$

where G is the vacancy Green's function and V is the perturbation. For a vacancy created at site $\vec{\nu}$ we have from (3.1)

$$G(\vec{m},\vec{n})=G^0(\vec{m},\vec{n})+V_0G^0(\vec{m},\vec{\nu})G(\vec{\nu},\vec{n})\,. \tag{3.2}$$

This equation can be solved to give

$$G(\vec{m},\vec{n})=G^0(\vec{m},\vec{n})+\frac{V_0G^0(\vec{m},\vec{\nu})G^0(\vec{\nu},\vec{n})}{1-V_0G^0(\vec{\nu},\vec{\nu})}\,. \tag{3.3}$$

Letting the perturbation potential V_0 tend to infinity we obtain for the vacancy Green's function

$$G(\vec{m},\vec{n})=G^0(\vec{m},\vec{n})-\frac{G^0(\vec{m},\vec{\nu})G^0(\vec{\nu},\vec{n})}{G^0(\vec{\nu},\vec{\nu})}\,. \tag{3.4}$$

In particular, the diagonal matrix elements are given by

$$G(\vec{m},\vec{m})=G^0(\vec{m},\vec{m})-\frac{G^0(\vec{m},\vec{\nu})G^0(\vec{\nu},\vec{m})}{G^0(\vec{\nu},\vec{\nu})}\,. \tag{3.5}$$

The local density of states, at site $\vec{m}$, is related to this Green's function by

$$n_{\vec{m}}(E)=(1/\pi)\,\mathrm{Im}\,G(\vec{m},\vec{m})\,, \tag{3.6}$$

where Im denotes the imaginary part of a complex function. The local density of states can be evaluated from Eqs. (3.5) and (3.6) by using the unperturbed Green's function (2.6) and the transformation (2.9). Figure 1 shows the results of such a numerical calculation. The interface considered in this case is one which is formed between two metals with $\Delta E_F=6E_1$. The vacancy was created on the interface plane ($\nu=0$), on the side of the metal with the higher Fermi energy. We take the vacancy to be at the origin of the plane $\nu=0$. Figures 1(a) and 1(b) show the local density of states at the nearest-neighbor site and the next-nearest-neighbor site on the same plane, $\nu=0$. Also shown

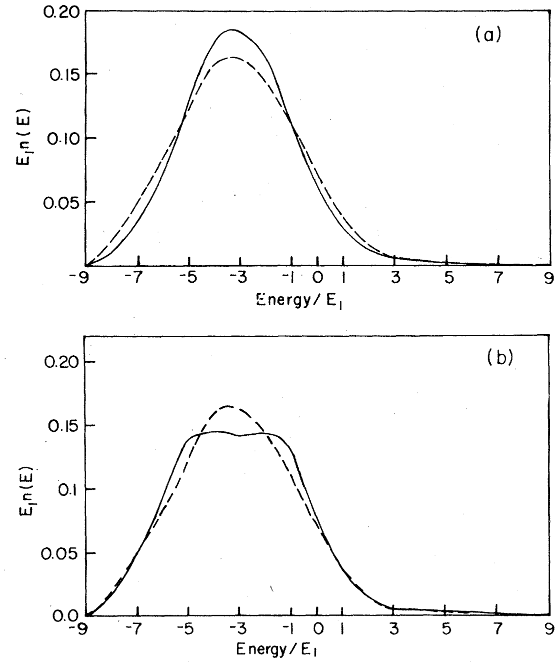

FIG. 1. Local density of states in the vicinity of a vacancy located at the interface plane $\nu=0$ of an interface with $\Delta E_F=6E_1$. The sites considered are nearest neighbors (a) and next nearest neighbors (b), both located on the plane $\nu=0$. Shown in a broken line is the corresponding local density of states of a coherent interface.

is the local density of states of the unperturbed interface. As can be seen from these figures, the presence of the vacancy introduces a significant change in the local density of states in its immediate vicinity. However, this change becomes small beyond the next nearest neighbors.

Let us turn now to the determination of the vacancy-formation energy. Since the presence of the interface destroys the translational symmetry perpendicular to the junction, this energy will depend on the distance of the vacancy from the interface.

The change in the total density of states associated with the creation of a vacancy on a site located on plane m is given by

$$\delta n^m(E) = (g/\pi)(\partial/\partial E)\,\mathrm{Im}\ln[\det(1 - G^0 V_{\vec{m}})]\,, \qquad (3.7)$$

where $V_{\vec{m}}$ is the corresponding perturbation necessary to create the vacancy, Eq. (2.10), and $g = 10$ is the degeneracy of the bands. Explicitly we have

$$\det(1 - G^0 V_{\vec{m}}) = 1 - V_0 G^0(\vec{m}, \vec{m})\,. \qquad (3.8)$$

Letting V_0 tend to infinity we obtain

$$\delta n^m(E) = (g/\pi)(\partial/\partial E)\arg G^0(\vec{m}, \vec{m})\,, \qquad (3.9)$$

where arg denotes the argument of a complex function. The corresponding change in the integrated density of states is given by

$$\delta N^m(E) = (g/\pi)\arg G^0(\vec{m}, \vec{m}) - g\,. \qquad (3.10)$$

In writing the above expression we take into account the fact that the Green's function $G^0(\vec{m}, \vec{m})$ is real and negative below the bands.

Using Eqs. (2.6) and (3.10) we determine the change in the integrated density of states $\delta N^m(E)$ for two types of interfaces, one for which $\Delta E_F = 2E_1$, and the other for which $\Delta E_F = 6E_1$. Figures 2 and 3 show the corresponding changes due to a vacancy in the metal having the higher Fermi level. The vacancies considered were created in two locations, at the interface layer $m = 0$ and at the next atomic layer $m = 1$. Also shown in these figures is the corresponding change in the integrated density of states due to the creation of a vacancy in the bulk. As can be seen from Figs. 2 and 3, the largest difference from the bulk values occurs, as expected, when the vacancy is closest to the interface (i.e., a vacancy at $m = 0$). In this case there is also a significant difference outside the bulk band. This difference is contributed by states tunneling from the other side of the interface. The change in the integrated density of states due to a vacancy in the third layer, not shown in Figs. 2 and 3, is almost identical to the bulk values.

The vacancy-formation energy is the energy necessary to displace an atom from its original lattice site to a bulk site far away from the interface, while leaving a vacancy at the original site. From the symmetry of the problem it is obvious that this energy will depend on the distance of the vacancy from the interface (and not on its transverse coordinate). Thus, we shall use E^m_{VF} to denote the formation energy of a vacancy on plane number m. This energy is given by

$$E^m_{\mathrm{VF}} = \int_{-\infty}^{E'_F} [\delta n^m(E) + n^0_a(E)]E\,dE\,, \qquad (3.11)$$

where $n^0_a(E)$ is the bulk density of states of metal a, shifted by the value of the dipole barrier, and $\delta n^m(E)$ is the change in density of states due to the creation of the vacancy. The fermi energy E'_F differs from E_F by a term which is $O(1/N)$, where N is the number of atoms in the system. This E'_F guarantees the charge neutrality of the vacancy. Expanding expression (3.11) to first order in $E'_F - E_F$ and integrating by parts gives

$$E^m_{\mathrm{VF}} = -\int_{-\infty}^{E_F} [\delta N^m(E) + N^0_a(E)]\,dE\,. \qquad (3.12)$$

In this equation $N^0_a(E)$ is the integrated bulk density of states. Using Eq. (3.10) for $\delta N^m(E)$ and Eq. (2.6) for the diagonal elements of the Green's function we can write the vacancy-formation energy as follows:

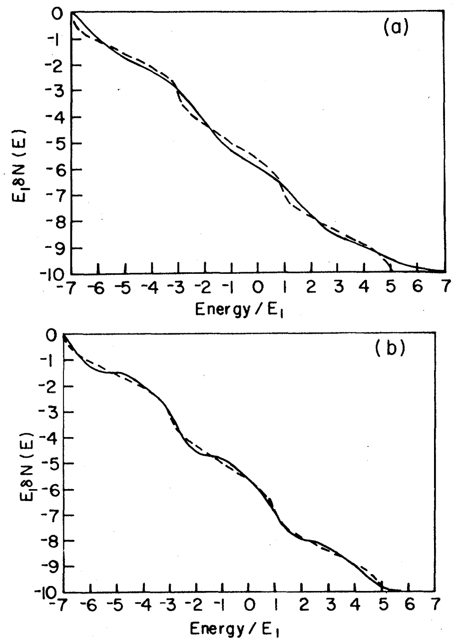

FIG. 2. Change in the integrated density of states due to a vacancy on the plane $m = 0$ (a) and the plane $m = 1$ (b) for an interface with $\Delta E_F = 2E_1$. Shown in a broken line is the corresponding change due to a vacancy in the bulk.

$$E_{\mathrm{VF}}^{m}=g(E_F^a+6E_1)-\frac{g}{\pi}\int_{-\infty}^{E_F}dE\,\arg\int\frac{d\vec{k}_{\parallel}}{(2\pi)^2}\left[\frac{i}{\mu_a}+\frac{1}{\mu_a+i\omega_a}\left(\frac{\omega_a+i\mu_a}{2E_1}\right)^{2m}\times\left(\frac{i\mu_a+\omega_a}{\mu_a}-\frac{8E_1^2 i}{4E_1^2+(\mu_a+i\omega_a)(\mu_b+i\omega_b)}\right)\right]$$
$$-\frac{g}{\pi}\int_{-\infty}^{E_F}\int_{-\infty}^{E}dE'\,\frac{d\vec{k}_{\parallel}}{(2\pi)^2}\,\mathrm{Im}\left(\frac{i}{\mu_a}\right)\,. \qquad (3.13)$$

We take now the case that metal a, where the vacancy is created, has a half-filled d band (i.e., 5 d electrons). Applying Eq. (3.13) we calculated the vacancy-formation energy for three vacancy locations, $m=0$, 1, and 2. The number of d electrons of the second metal, n_b, was allowed to vary continuously between an empty band, $n_b=0$, and a full d band, $n_b=10$. Figure 4 shows the variation of the vacancy-formation energy as a function of the vacancy position and the number of electrons of the second metal forming the interface. The point $n_b=5$ gives the vacancy-formation energy of a bulk half-filled band metal. This is of course position independent, and therefore all three curves of Fig. 4 intersect at the same point, where $n_b=5$. As can also be seen from this figure, the vacancy energy is the lowest at the interface plane $m=0$. Therefore, once a vacancy is formed it will tend to migrate towards the interface. However, to reach the interface itself it will have to tunnel through a barrier, since the energy at $m=1$ is always higher than the bulk value. As can be seen from Fig. 4 the vacancy-formation energy is an oscillatory function of the distance from the interface, reminiscent of the Ruderman-Kittel[13] interaction.

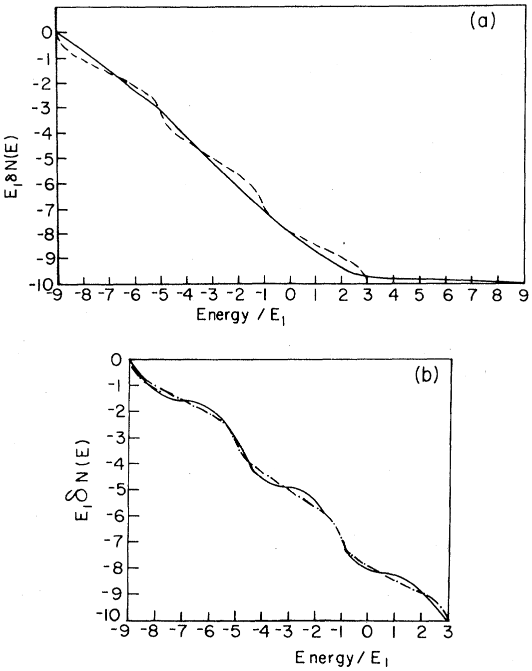

FIG. 3. Change in the integrated density of states due to a vacancy on the plane $m=0$ (a) and the plane $m=1$ (b) for an interface with $\Delta E_F=6E_1$. Shown in a broken line is the corresponding change due to a vacancy created in the bulk.

IV. VACANCY-VACANCY INTERACTION

The presence of a vacancy in the system polarizes the medium in its immediate vicinity. If a second vacancy is created close to the first one, the polarization of the medium will lead to an indirect interaction between the two vacancies. In this section we discuss this interaction as a function of the position of the vacancies. Since the presence of the interface destroys the translational symmetry, the vacancy-vacancy interaction will also depend on their position relative to the interface.

The change in the density of states due to the presence of a single vacancy at a given site $\vec{m}$ was determined in the preceding section, Eq. (3.11). If the vacancies were not interacting, and a second vacancy was created at another site $\vec{n}$, then the total change in the integrated density of states would have been just the sum of the corresponding changes caused by the two isolated vacancies; i.e.,

$$\delta N^0(E)=(g/\pi)\arg[G^0(\vec{m},\vec{m})G^0(\vec{n},\vec{n})]-2g\,. \qquad (4.1)$$

However, the actual change in the intergrated den-

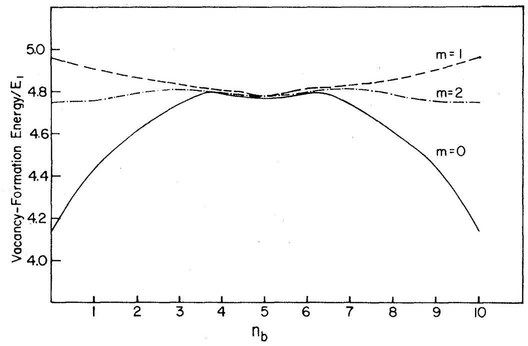

FIG. 4. Vacancy-formation energy as a function of the number of d electrons and its position relative to the interface for the family of interfaces discussed in the text.

sity of states differs from the noninteracting expression (4.1). To determine this change we shall create the two vacancies in succession. The change due to the creation of the first vacancy at site $\vec{m}$ is given by Eq. (3.10). The presence of this vacancy polarizes the medium and induces a change in the local Green's functions, given by Eq. (3.4). Applying this equation and Eq. (3.1), we obtain that the change in the integrated density of states caused by the presence of two vacancies, one at $\vec{m}$ and the other at $\vec{n}$, is given by

$$\delta N(E) = (g/\pi)\arg[G^0(\vec{m},\vec{m})G^0(\vec{n},\vec{n}) - G^0(\vec{m},\vec{n})G^0(\vec{n},\vec{m})] - 2g\,. \tag{4.2}$$

Comparing this expression with Eq. (4.1) above shows that the change in $N(E)$ due to the vacancy-vacancy interaction is

$$\Delta N_{\vec{m},\vec{n}}(E) \equiv \delta N(E) - \delta N^0(E) = \frac{g}{\pi}\arg\left(1 - \frac{G^0(\vec{m},\vec{n})G^0(\vec{n},\vec{m})}{G^0(\vec{m},\vec{m})G^0(\vec{n},\vec{n})}\right)\,. \tag{4.3}$$

Figure 5 shows the change in the integrated density of states due to the vacancy-vacancy interaction. The interface considered is one formed between an empty and a half-filled band metal. The two vacancies are taken to be on the interface plane, $m=0$, of the half-filled band metal. The two cases described refer to nearest-neighbor and next-nearest-neighbor vacancies.

From the knowledge of $\Delta N_{\vec{m},\vec{n}}(E)$ one can easily determine the vacancy-vacancy interaction energy. This is given by

$$E(\vec{m},\vec{n}) = -\int_{-\infty}^{E_F} \Delta N_{\vec{m},\vec{n}}(E)\,dE = -\frac{g}{\pi}\int_{-\infty}^{E_F} \arg\left(1 - \frac{G^0(\vec{m},\vec{n})G^0(\vec{n},\vec{m})}{G^0(\vec{m},\vec{m})G^0(\vec{n},\vec{n})}\right)\,. \tag{4.4}$$

For the numerical calculation we again consider the interface treated earlier in this section (i.e., the two metals having 0 and 5 d electrons, respectively). Of the two vacancies one is taken to be at the origin of the $m=0$ plane. Figure 6 describes the behavior of the interaction energy as a function of the distance between the two vacancies in the [100], [010], and the [011] directions. This interaction has an oscillatory character very similar to the Ruderman-Kittel-type[13] interaction between two point imperfections in the bulk of a free-electron gas. The origin of these oscillations is the sharpness of the Fermi surface. The easiest way to see how such oscillations arise is to look at the simpler one-dimensional interface. In this case it follows from Eq. (2.6a) that inside

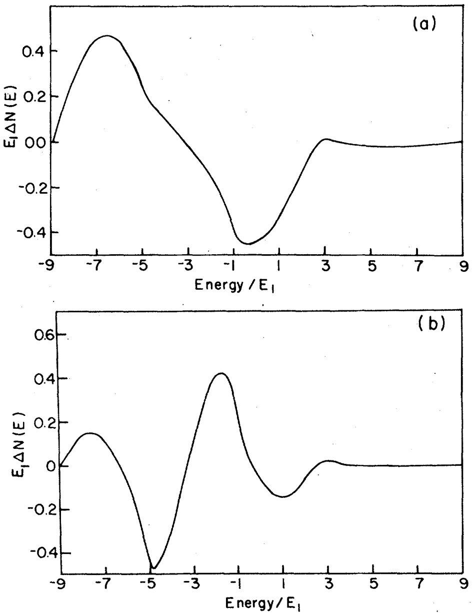

FIG. 5. Change of the integrated density of states due to vacancy-vacancy interaction: (a) nearest neighbors, (b) next-nearest neighbors. The two vacancies are located on the plane $m=0$.

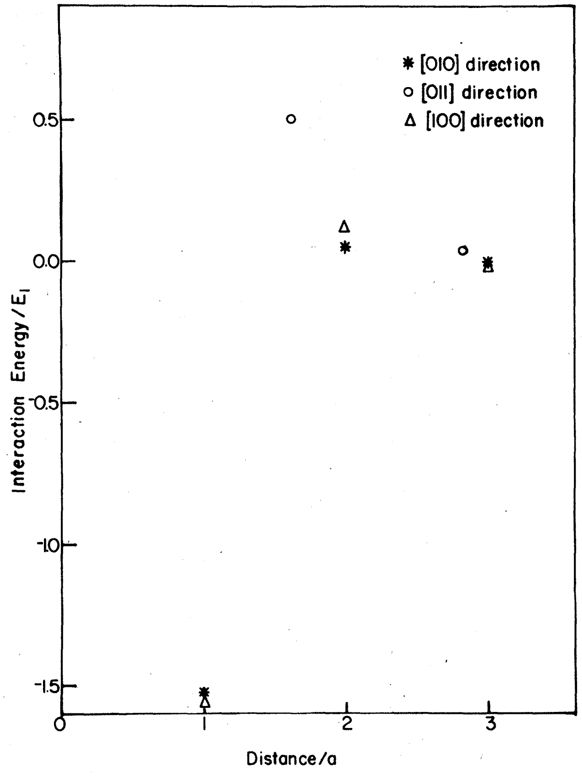

FIG. 6. Vacancy-vacancy interaction energy as a function of their distance, in the [100], [010], and [011] directions, for an interface formed between an empty and a half-filled d-band metal. One of the vacancies is always taken to be on the $m=0$ plane.

the bands the dependence of G^0 $(0,n)$ on the distance n is via a factor of the form $e^{i\theta(E)n}$, where the real angle $\theta(E)$ is given by

$$\theta(E)=\arctan\left(\frac{\{4-[(E+\Delta V)/E_1]^2\}^{1/2}}{(E+\Delta V)/E_1}\right). \qquad (4.5)$$

As the energy varies from the botton to the top of the band θ varies from $-\pi$ to 0. Equation (4.3) shows that the change in the integrated density of states is proportional in this case to terms oscillating like $\cos(2n\theta)$ or $\sin(2n\theta)$, and the vacancy-vacancy interaction will thus be proportional to an oscillatory function of the form $\cos[2n\theta(E_F)]$ or $\sin[2n\theta(E_F)]$, where $\theta(E_F)$ is the value of θ evaluated at the Fermi energy. For the one-dimensional case the shifted bulk band is given by

$$E+\Delta V=-2E_1\cos(ka). \qquad (4.6)$$

Close to the bottom edge of the band we can write

$$E+\Delta V\cong -2E_1[1-\tfrac{1}{2}(ka)^2], \qquad (4.7)$$

and the corresponding angle θ is therefore

$$\theta(E)\cong -\pi+ka.$$

Thus, for a nearly empty band, where the effective-mass approximation (4.7) applies, the vacancy-vacancy interaction energy will be proportional to terms oscillating like $\cos(2k_Fna)$ [or $\sin(2k_Fna)$], where k_F is the Fermi momentum. Thus, the oscillations have a spatial wavelength of $2k_F$, which is the typical wavelength of the Ruderman-Kittel interaction or any other Friedel oscillations.

As can be seen from Fig. 6 the range of the interaction is about three lattice spacings. Whereas the nearest-neighbor interaction is attractive, the next-nearest-neighbor interaction has a repulsive character.

V. DISCUSSION

The properties of vacancies near a bimetallic interface were evaluated in the preceding sections. As can be seen from these results, the effect of a vacancy on the various electronic properties has a typical range of about three atomic layers. Within this range the corresponding energies exhibit an oscillatory behavior whose origin is similar to the one of the well-known Ruderman-Kittel interaction.

As was shown explicitly in Sec. III the vacancy-formation energy E_{VF}, is an oscillatory function of the vacancy's distance from the interface. For the specific family of interfaces considered in this article the vacancy attains its minimum energy as it reaches the interface. Therefore, an attempt to "clean" the interface from vacancies by heating the junction will fail, since the vacancies will tend to migrate towards the interface. It is interesting to note that the largest energy gain due to such a migration is about $0.6E_1$ for the interfaces considered. Since E_1 is typically 0.5 eV, this energy gain is about 0.3 eV or about 13% of the vacancy-formation energy. We also note that the barrier height, through which the vacancy has to tunnel in order to reach the interface in the case under consideration, is of the order of 0.1 eV.

However, the opposite situation, where vacancies are repelled from the interface, is also possible in principle for other types of interfaces. Thus, the answer to the question whether heat treatment improves or degrades the properties of a given interface depends on the specific type of junction under consideration.

The possibility of getting a delocalized vacancy, a defecton, due to a finite hopping amplitude, was considered originally by Andreev and Lifshitz.[14] We note that the breaking of the translational symmetry of the system due to the presence of the interface is a possible mechanism for the localization of such defectons, at least perpendicular to the interface.

As was shown in Sec. III, the vacancy-vacancy interaction has also an oscillatory nature, being attractive in some regions and repulsive in others. The maximum attractive interaction, for the interface considered, is of the order of $1.5E_1$, or 0.75 eV. This is quite a large energy, amounting to about $\frac{1}{3}$ of the vacancy-formation energy. The highest repulsion energy is between closest neighbors along the [011] direction, and is equal to $0.5E_1$ or 0.25 eV, about 10% of E_{VF}.

The oscillatory behavior of the vacancy-vacancy interaction allows in principle for the formation of a super lattice of vacancies. For the interfaces considered in this article, this interaction is most attractive for nearest-neighbor vacancies. It thus seems favorable that the lattice parameter of the super lattice will be the same as of the original lattice, although this needs a more detailed calculation. In general one would, however, expect that such a possible super lattice will have a larger lattice parameter than the underlying crystal structure.

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