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ELECTRONIC ENERGIES OF INTERACTION OF POINT DEFECTS WITH INTERFACES AND GRAIN BOUNDARIES

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The electronic energies of interaction of a point defect with interfaces and grain boundaries are calculated, as a function of the distance x_{03} between the point defect and the corresponding planar defect. These interaction energies are shown to have the same type of oscillations as the corresponding local electronic densities. Therefore the electronic interactions more significantly affect the energy of segregation of point defects towards interfaces when x_{03} is in the near vicinity of these interfaces, while at large distances the contribution of elastic interactions can dominate.

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Grain boundary segregation is an area of intense interest since solute atoms concentrating at grain boundaries can alter drastically the properties of bulk polycrystalline materials. Elastic and electronic interactions are the major contributions to equilibrium segregation of impurities to grain boundaries in simple metals.

In the previous publication [1], analytic expressions were reported for the elastic energy of interaction of a point defect with a planar defect. The excess elastic energy of the point defect in the vicinity of the planar defect was found to be short range and to vary as $1/d^4$ where d is the distance from the planar defect. This energy was expected to be a leading contribution to segregation.

The electronic energy of interaction of a solute atom with a grain boundary is believed to offer an insufficient driving force for segregation. Friedel [2] presented a variation of the electronic energy exhibiting damped oscillations as a function of the distance. Atomistic calculations based on pair potentials or on tight-binding models have been performed to determine the excess energy of solute atoms at

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different sites in the vicinity of surfaces [3, 4] or near a grain boundary [5]. The density functional formalism was also applied to obtain the electronic density near a planar defect and the energy of a grain boundary [6].

The purpose of this paper is to obtain within a simple but general model the excess energy of a point defect near an interface between two metals M_1 and M_2 , or near a planar defect modelled as a thin slab of metal M_2 sandwiched between two semi-infinite perfect crystals of metal M_1 . This energy will be expressed as a simple integral which is easy to evaluate. Furthermore the Green function method used in this work can easily be extended to more complicated heterostructures. The calculations are conducted in the nearly free electron model, with step barriers at the interfaces.

The perturbation potential due to solute atom located at r_0 is assumed to be a point-like potential

$$V(r) = A_0 \delta(r - r_0), \quad (1)$$

where $\delta(r)$ is the usual delta function and A_0 defines the strength of the perturbation.

The correction to a non-degenerated electronic energy level of the system due to this potential is written, to the first order in the perturbation $V(r)$, in the form

$$\varepsilon(r_0, E) = \langle \Psi | V | \Psi \rangle \quad (2)$$

where $|\Psi\rangle$ is an eigenvector of the unperturbed system associated with the energy E . Introducing Eq. (1) in (2) gives

$$\varepsilon(r_0, E) = A_0 n_0(r_0, E), \quad (3a)$$

where $n_0(r_0, E)$ is the contribution of the electrons with energy E to the electronic density at location r_0 in the unperturbed interface or sandwich system.

Furthermore, the electronic density $n_0(r_0, E)$ can be advantageously determined from the imaginary part of the Green function $g(r_0, r_0, E)$ of the unperturbed system by the relation

$$n(r_0, E) = -\frac{1}{\pi} \text{Im} g(r_0, r_0, E). \quad (3b)$$

Then the total energy of the point defect in the M_1 - M_2 or in the M_1 - M_2 - M_1 composite system is obtained at 0 K by summing $\varepsilon(r_0, E)$ over all possible states inside the Fermi surface

$$\varepsilon(r_0) = A_0 n(r_0), \quad (4a)$$

where $n(r_0)$ is the electronic density at location r_0

$$n(r_0) = -\frac{1}{\pi} \text{Im} \int^{E_F} dE g(r_0, r_0, E). \quad (4b)$$

The calculation of the Green function is first performed in the two-dimensional space parallel to the interfaces by using the interface response theory of Ref. [7]. This means that we express the elements $g(k_{\parallel}; x_{03}; x'_{03}; E)$ of the Green function,

where k_{\parallel} is the wave vector parallel to the interfaces and x_{03} is the direction perpendicular to them. These expressions are given in the Appendix 1. Then

$$n(r_0) = -\frac{1}{\pi} \text{Im} \int^{E_F} dE \int \frac{d^2 k_{\parallel}}{(2\pi)^2} g(k_{\parallel}; x_{03}; x_{03}; E). \quad (4c)$$

In our calculation the metals M_1 and M_2 involved in the M_1 - M_2 interface system or in the M_1 - M_2 - M_1 planar defect are characterized by their ground energies E_1 , E_2 and their effective masses m_1 , m_2 . In the nearly free electron approximation these parameters are related to the bulk electronic density n_i in metal i by the relation

$$E_F - E_i = \frac{\hbar^2}{2m_i} \left(\frac{3n_i}{8\pi} \right)^{2/3} \quad i = 1, 2. \quad (5)$$

The Fermi levels of both metals are aligned in the composite system at the energy E_F . We also introduce the quantities

$$\alpha_i^2 = k_{\parallel}^2 - \frac{(E - E_i)}{B_i} \quad (6a)$$

with

$$B_i = \frac{2m_i}{\hbar^2}. \quad (6b)$$

For the sake of simplicity, we chose the effective mass of the electron to be the same in both media M_1 and M_2 ($B_1 = B_2 = B$).

Finally the geometries of the systems are defined as follows. In the interface problem, the metal M_1 (M_2) fills the negative (positive) x_3 half-space. In the planar defect system, the slab M_2 fills the region $-X < x_3 < +X$, where $x_3 = \pm X$ define the locations of the interfaces.

Let us assume that E_1 is below E_2 which means that the electron density is smaller in material M_2 than in material M_1 . This is expected to be the case in high angle grain boundaries which are dilated regions showing lower atomic densities than in the bulk. The multiple integral in Eq. (4c) can be simplified by changing the variables $u^2 = (E - E_i)/B_1 - k_{\parallel}^2$ and $k^2 = 2m(E - E_1)/\hbar^2$ and by inverting the order of integration over u and k . After some algebra, we obtain $n(r_0)$ as a simple integral of the form

$$n(x_{03}) = \frac{1}{2\pi^2} \int_0^{k_F} (k_F^2 - u^2) \text{Im}g(u, x_{03}) u du. \quad (7)$$

The expression of $g(u, x_{03})$ which is dependent upon the location x_{03} of the impurity is given in Appendix 2.

As the first application of this calculation, Fig. 1 presents the variation of $n(x_{03})$ near a bimetallic interface M_1 - M_2 . The bulk charge density in metals M_1 and M_2 are chosen in order to simulate an Al-Ag system. Apart from a rapid variation near the interface, the charge density shows decaying oscillations with period π/k_F before reaching the bulk value on each side of the interface. In a self-consistent calculation as in Ref. [8], the oscillations are actually less pronounced than those in Fig. 1.

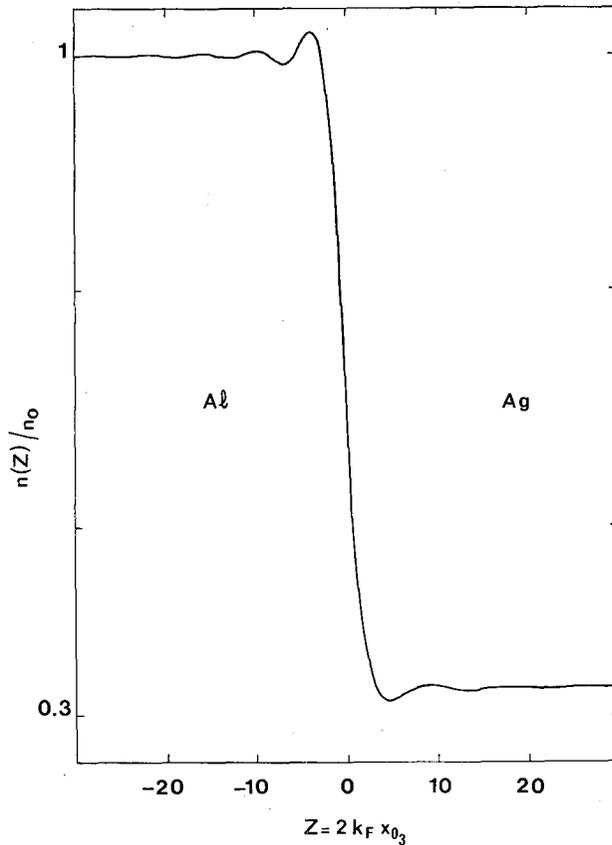


Fig. 1. Electronic density near a Al-Ag interface, normalised to the bulk electronic density in Al.

In Fig. 2, we present the behaviour of the electronic density in a Al crystal containing a planar defect. The electronic density inside the planar defect is chosen to be 20% smaller than in the bulk crystal in order to simulate a smaller atomic density inside a grain boundary. The curves in Fig. 2 refer to different thicknesses $2X$ of the planar defect.

Again one can notice a rapid variation of the electronic density in the near vicinity of the interfaces. Inside a relatively thick planar defect $n(x_{03})$ shows decaying oscillations before reaching a limiting value; in contrast, in a very thin planar defect $n(x_{03})$ behaves rather parabolically with a minimum at $x_{03} = 0$ which is higher than in the thick grain boundary case.

Outside the grain boundary, the behaviour of the electronic density is qualitatively similar to that in the bimetallic system, except for a very thin planar defect where the charge density is influenced by the presence of both interfaces.

As a conclusion, we can notice that at large distances from the planar defect,

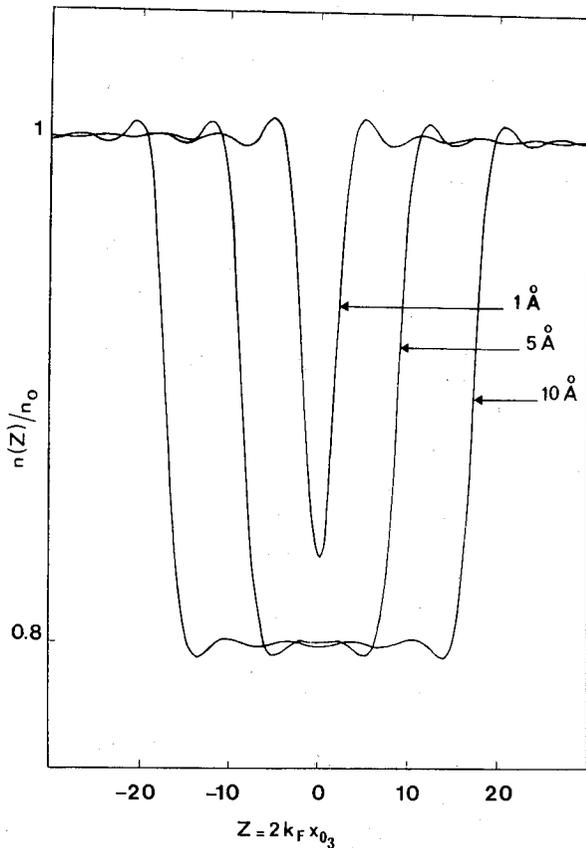


Fig. 2. Electronic density near a planar defect in an Al crystal, for three different thicknesses (1, 5 and 10 Å) of the planar defect. The density is normalised to the bulk density of Al. The atomic density in the grain boundary is assumed to be 20% lower than in the bulk crystal.

the electronic energy shows an attenuated sinusoidal variation which gives rise to an oscillating driving force changing sign every fraction of an interatomic distance; therefore this mechanism does not provide a sufficient driving force for segregation of impurities. In contrast, at very short distances, that is within a few atomic radii from the grain boundary core, the electronic energy may represent a significant contribution to the energy of segregation. This is in accordance with measurements of the extent of the equilibrium grain boundary segregation which indicate the limitation of the segregation phenomenon to a few atomic layers at the grain boundary core [9].

Finally let us mention that although only qualitative results can be expected from our simple approach, the method of calculation can easily be extended to other heterostructures of more complex geometries.

Appendix 1

Here we report the Green function $g(k_{\parallel}, x_3, x'_3; E)$ for a M_1 - M_2 interface system and a M_1 - M_2 - M_1 sandwich system in the approximation of the nearly free electrons.

1) M_1 - M_2 interface system

— In the medium M_1 ($x_3, x'_3 \leq 0$)

$$g(k_{\parallel}, x_3, x'_3; E) = -\frac{1}{2\alpha_1 B_1} \left[e^{-\alpha_1 |x_3 - x'_3|} + \frac{\alpha_1 B_1 - \alpha_2 B_2}{\alpha_1 B_1 + \alpha_2 B_2} e^{\alpha_1 (x_3 + x'_3)} \right];$$

— In the medium M_2 ($x_3, x'_3 \geq 0$)

$$g(k_{\parallel}; x_3, x'_3, E) = -\frac{1}{2\alpha_2 B_2} \left[e^{-\alpha_2 |x_3 - x'_3|} - \frac{\alpha_1 B_1 - \alpha_2 B_2}{\alpha_1 B_1 + \alpha_2 B_2} e^{-\alpha_2 (x_3 + x'_3)} \right].$$

2) M_1 - M_2 - M_1 sandwich system:

— In the medium M_1 with $x_3, x'_3 \leq -X$

$$g(k_{\parallel}; x_3, x'_3, E) = -\frac{e^{-\alpha_1 |x_3 - x'_3|}}{2\alpha_1 B_1} + \frac{e^{\alpha_1 (x_3 + x'_3 + 2X)}}{2\alpha_1 B_1} - \frac{\alpha_1 B_1 \operatorname{th}(2\alpha_2 X) + \alpha_2 B_2}{W(k_{\parallel}, E)} e^{\alpha_1 (x_3 + x'_3 + 2X)};$$

— In the medium M_2 ($-X \leq x_3, x'_3 \leq +X$)

$$g(k_{\parallel}; x_3, x'_3, E) = -\frac{e^{-\alpha_2 |x_3 - x'_3|}}{2\alpha_2 B_2} + \frac{1}{2\alpha_2 B_2 \operatorname{sh}(2\alpha_2 X)} \left\{ \operatorname{ch}[\alpha_2 (x_3 + x'_3)] - e^{-2\alpha_2 X} \operatorname{ch}[\alpha_2 (x_3 - x'_3)] \right\} - \frac{1}{2W(k_{\parallel}, E) \operatorname{sh}^2(2\alpha_2 X)} \left\{ [\alpha_1 B_1 \operatorname{th}(2\alpha_2 X) + \alpha_2 B_2] \times \left[\operatorname{ch}[\alpha_2 (x_3 + x'_3 - 2X)] + \operatorname{ch}[\alpha_2 (x_3 + x'_3 + 2X)] - 2\operatorname{ch}[\alpha_2 (x_3 - x'_3)] \right] + \frac{\alpha_2 B_2}{\operatorname{ch}(2\alpha_2 X)} [\operatorname{ch}[\alpha_2 (x_3 - x'_3 + 2X)] + \operatorname{ch}[\alpha_2 (x_3 - x'_3 - 2X)] - 2\operatorname{ch}[\alpha_2 (x_3 + x'_3)] \right\};$$

— In the medium M_1 with $x_3, x'_3 \geq +X$

$$g(k_{\parallel}; x_3, x'_3, E) = -\frac{e^{-\alpha_1 |x_3 - x'_3|}}{2\alpha_1 B_1} + \frac{e^{-\alpha_1 (x_3 + x'_3 - 2X)}}{2\alpha_1 B_1} - \frac{\alpha_1 B_1 \operatorname{th}(2\alpha_2 X) + \alpha_2 B_2}{W(k_{\parallel}, E)} e^{-\alpha_1 (x_3 + x'_3 - 2X)}.$$

In these expressions the denominator $W(k_{\parallel}, E)$ is given by

$$W(k_{\parallel}, E) = (\alpha_1^2 B_1^2 + \alpha_2^2 B_2^2) \operatorname{th}(2\alpha_2 X) + 2\alpha_1 B_1 \alpha_2 B_2.$$

Appendix 2

In this appendix, we give the expressions of $g(u, x_{03})$ appearing in Eq. (7) according to the location x_{03} of the impurity.

1) M_1 - M_2 interface system:

For $x_{03} \leq 0$

$$g(u, x_{03}) = -\frac{i}{2uB} \left(1 + \frac{i u + \alpha_2}{i u - \alpha_2} e^{-2iu x_{03}} \right),$$

where

$$\alpha_2 = \begin{cases} \sqrt{k_0^2 - u^2} & \text{if } u \leq k_0, \\ -i\sqrt{u^2 - k_0^2} & \text{if } u \geq k_0, \end{cases}$$

and $k_0 = \sqrt{(E_2 - E_1)/B}$.

For $x_{03} \geq 0$

$$g(u, x_{03}) = -\frac{1}{2\alpha_2 B} \left(1 + \frac{i u + \alpha_2}{i u - \alpha_2} e^{-2\alpha_2 x_{03}} \right).$$

2) M_1 - M_2 - M_1 sandwich system

For $x_{03} \leq -X$

$$g(u, x_{03}) = \frac{-i(1 - e^{-2iu(x_{03}+X)})}{2uB} - \frac{(\alpha_2 - i\text{uth}(2\alpha_2 X)) e^{-2iu(x_{03}+X)}}{B[(\alpha_2^2 - u^2)\text{th}(2\alpha_2 X) - 2iu\alpha_2]}.$$

For $-X \leq x_{03} \leq +X$

$$g(u, x_{03}) = -\frac{1}{2\alpha_2 B} + \frac{1}{2\alpha_2 B \text{sh}(2\alpha_2 X)} [\text{ch}(2\alpha_2 x_{03}) - e^{-2\alpha_2 X}] - \frac{1}{B \text{sh}^2(2\alpha_2 X) [(\alpha_2^2 - u^2)\text{th}(2\alpha_2 X) - 2iu\alpha_2]} \times \left\{ (-i\text{uth}(2\alpha_2 X) + \alpha_2) [\text{ch}(2\alpha_2 x_{03}) \text{ch}(2\alpha_2 X) - 1] + \alpha_2 \left[1 - \frac{\text{ch}(2\alpha_2 x_{03})}{\text{ch}(2\alpha_2 X)} \right] \right\}.$$

For $x_{03} \geq +X$

$$g(u, x_{03}) = \frac{-i[1 - e^{2iu(x_{03}-X)}]}{2uB} - \frac{[\alpha_2 - i\text{uth}(2\alpha_2 X)] e^{2iu(x_{03}-X)}}{B[(\alpha_2^2 - u^2)\text{th}(2\alpha_2 X) - 2iu\alpha_2]}.$$

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