



# Electronic contribution to the point defect/curved-interface binding energy. Effect on segregation of curved interfaces

P A Deymier, *Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, USA*

and

J O Vasseur, *Equipe de Dynamique des Interfaces, Laboratoire de Dynamique et Structure des Matériaux Moléculaires, URA CNRS n°801-UFR de Physique, Université de Lille I, 59655 Villeneuve d'Ascq, Cédex, France*

*The electronic contribution to the driving force for segregation to a curved-interface between a cylindrical fiber of insulator embedded in a metal matrix is calculated. The solute/curved-interface binding energy is shown to vary as the inverse of the radius of curvature of the interface in the limit of a small radius. This result implies that the propensity for segregation of curved interfaces is larger than that of planar interfaces.*

## 1. Introduction

The phenomenon of segregation of solute atoms to interfaces plays an important role in determining the bulk properties of polycrystalline materials. It is now well recognized that the extent of solute segregation is affected by the physical characteristics of the interface. To date most experimental and theoretical investigations have concentrated on planar interfaces. Very little attention has been given to the effect of interfacial morphology on segregation. Of particular interest is the relationship between the interface curvature and the driving forces for solute segregation. Experimental evidence for such a relationship is scarce but indications of curvature effects on interfacial segregation exist<sup>1</sup>.

The driving forces for solute segregation in metallic alloys include elastic and electronic contributions. In this paper we introduce a simple model of a curved interface which enables the calculation of the electronic contribution to the binding energy of a heterovalent impurity to the interface. The system is composed of a metallic matrix containing a cylindrical inclusion of insulating material. This model is therefore only applicable to metal/insulator interfaces such as those present in metal-matrix/insulator-fiber composites. A first order approximation for the binding energy of a single solute atom in a metallic medium in terms of the medium Green's function is presented in Section 2. In Section 3 we report the calculation of the Green's function of the metallic medium containing a cylindrical inclusion of insulating material. The effect of the curvature of the cylindrical inclusion on the propensity for segregation of the impurity atom is discussed in Section 4. Finally, general conclusions regarding the phenomenon of segregation to curved interfaces are drawn in Section 5.

## 2. Electronic contribution to solute energy

The purpose of this section is to obtain within a simple model the electronic contribution to the energy of a point defect in some metallic medium. The metallic medium is described within the nearly free electron model, thus limiting the applicability of the model to simple metals.

We first model a heterovalent solute atom immersed in the medium at some position  $\vec{r}_0$  as a perturbing potential in the form<sup>2</sup>:

$$V(\vec{r}) = A\delta(\vec{r} - \vec{r}_0), \quad (1)$$

where  $\delta$  is the usual delta function, and  $A$  a constant measuring the strength of the perturbation. In the rest of this paper we will consider only weak perturbations. The correction to a non-degenerate electronic level of the medium resulting from the perturbing potential is expressed to first order in the form:

$$\varepsilon(\vec{r}_0, E) = \langle \psi | V | \psi \rangle, \quad (2)$$

where  $|\psi\rangle$  is an eigenvector of the unperturbed medium associated with the energy  $E$ . Substituting equation (1) into equation (2) yields:

$$\varepsilon(\vec{r}_0, E) = An_0(\vec{r}_0, E). \quad (3)$$

The quantity  $n_0(\vec{r}_0, E)$  corresponds to the contribution of electrons with energy  $E$  to the electronic density at the location  $\vec{r}_0$  in the unperturbed medium. This latter equation is particularly useful as the electronic density  $n_0(\vec{r}_0, E)$  can be advantageously determined from the imaginary part of the Green's function

$g(\vec{r}_o, \vec{r}_o, E)$  of the unperturbed medium through the following relation:

$$n_o(\vec{r}_o, E) = -\frac{1}{\pi} \text{Im} g(\vec{r}_o, \vec{r}_o, E). \quad (4)$$

The total electronic density at the point  $\vec{r}_o$  can then be obtained at O K by integrating  $n_o(\vec{r}_o, E)$  over all possible states inside the Fermi surface:

$$n_o(\vec{r}_o) = -\frac{2}{\pi} \text{Im} \int^{E_F} dE g(\vec{r}_o, \vec{r}_o, E). \quad (5)$$

The factor 2 in equation (5) is inserted to account for the spin degeneracy.

The total energy of the point defect located in the medium at  $\vec{r}_o$  is:

$$\varepsilon(\vec{r}_o) = A n_o(\vec{r}_o). \quad (6)$$

The preceding relationship enables us to evaluate the electronic contribution to the energy of an impurity by simply calculating the electronic density function.

### 3. Green's function of medium with curved interface

The model medium with a curved interface, which we consider in this paper, is a composite medium constituted of a metallic matrix with an infinitely long cylinder of insulating material oriented along some axis  $Z$ . The radius of the cylinder is denoted by  $R$ . The Green's function of the metallic medium in the composite medium is determined within the framework of the interface response theory of continuous media<sup>3</sup>. The Green's function  $g(\vec{r}, \vec{r}')$  at any two points  $(\vec{r}, \vec{r}')$  in the space,  $D$ , spanned by the metallic medium is given by:

$$g(DD) = G(DD) - G(DM)G^{-1}(MM)G(MD) + G(DM)G^{-1}(MM)g(MM)G^{-1}(MM)G(MD), \quad (7)$$

where  $M$  means that  $\vec{r}$  and  $\vec{r}'$  are limited to the domain of the interface between the metal and the insulator.  $G(\vec{r}, \vec{r}')$  is the Green's function of an infinite medium,  $g(MM)$  is the interface response function of the composite or, in other words, the Green's function of the composite medium limited to points on the interface. Since there are no electronic states at the interface between the metal and the insulator, the interface response function,  $g(MM)$ , vanishes and the Green's function of the metallic medium is easily evaluated in terms of the Green's function of an infinite metallic medium as:

$$g(DD) = G(DD) - G(DM)G^{-1}(MM)G(MD). \quad (8)$$

The Green's function of an infinite metallic medium within the approximation of the nearly free electron is solution of the equation:

$$[E - H(\vec{r})] \cdot G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'), \quad (9)$$

where  $E$  is the energy and  $\delta(\vec{r} - \vec{r}')$  is the Dirac function. The Hamiltonian,  $H$ , of the metal is given by:

$$H(\vec{r}) = -\frac{\hbar^2}{2m} \Delta + E_m, \quad (10)$$

where  $E_m$  is the constant potential energy in the metal and  $\hbar$  the reduced Planck's constant.

Since the infinite medium has translational symmetry along the  $Z$  axis, the Green's function can be Fourier analyzed:

$$G(\vec{r}, \vec{r}') = \int \frac{dk_z}{2\pi} G(\vec{r}_p, \vec{r}'_p, k_z) e^{ik_z(z-z')} \quad (11)$$

where  $\vec{r}_p$  and  $\vec{r}'_p$  are two dimensional vectors perpendicular to the  $Z$  axis. With this Fourier transformation, equation (9) reduces to:

$$B[\Delta_p + k_z^2]G(\vec{r}_p, \vec{r}'_p, k_z) = \delta(\vec{r}_p - \vec{r}'_p), \quad (12)$$

where  $B = \hbar^2/2m$ ;  $k_z$  being the component of the wave vector  $\vec{k}$  along the  $Z$  axis,  $\Delta_p$  is the two dimensional Laplacian. The quantity,  $k$ , is defined by  $k^2 = (E - E_m)/B - k_z^2$ .

The symmetry of our problem suggests the use of polar coordinates. We separate the angular and radial coordinates by expanding the Green's function in the form:

$$G(\vec{r}, \vec{r}', k_z) = \sum_{m=-\infty}^{+\infty} \frac{1}{2\pi} e^{im(\varphi-\varphi')} G_m(r, r', k_z). \quad (13)$$

Introducing equation (13) into equation (12) expressed in polar coordinates and making use of the orthogonal properties of the set  $e^{im\varphi}$ , we obtain:

$$B \left[ \frac{1}{r} \frac{d}{dr} \left( r \frac{dG_m}{dr} \right) + \left( k^2 - \frac{m^2}{r^2} \right) G_m \right] = \frac{\delta(r-r')}{r}. \quad (14)$$

The solutions to this equation are<sup>4</sup>:

$$G_m(r, r', k_z) = -\frac{\pi}{2B} i \begin{cases} J_m(kr) H_m(kr') & \text{if } r \leq r' \\ J_m(kr') H_m(kr) & \text{if } r \geq r' \end{cases}, \quad (15)$$

where  $J_m$  and  $H_m$  are the Bessel and Hankel functions of order  $m$ , respectively.

Equation (8) can now be used to evaluate the radial part of the Green's function of the metallic medium with a cylindrical interface. Here, the space of the interface,  $M$ , is reduced to the radius  $R$ . The Green's function at  $r' = r$  is given by:

$$g_m(r, r) = G_m(r, r) - G_m(r, R) G_m^{-1}(R, R) G_m(R, r). \quad (16)$$

In equation (16) we have dropped the variable  $k_z$  for the sake of simplicity; the dependence on  $k_z$  is now considered implicit in the parameter  $k$ .

Inserting the appropriate solutions (15) into equation (16) yields:

$$g_m(r, r) = -\frac{\pi}{2B} i H_m(kr) \left\{ J_m(kr) - J_m(kR) \frac{H_m(kr)}{H_m(kR)} \right\}. \quad (17)$$

The relationship,  $H_m = J_m + iY_m$  between the Hankel functions and the Bessel functions is used to extract the imaginary part of the radial Green's function in equation (17):

$$\text{Im} g_m(r, r) = -\frac{\pi}{2B} \left\{ \frac{[Y_m(kr)J_m(kR) - J_m(kr)Y_m(kR)]^2}{J_m^2(kR) + Y_m^2(kR)} \right\}. \quad (18)$$

To calculate the electronic density in the vicinity of the metal/insulator interface we only need the imaginary part of the radial Green's function since the angular variable  $\phi' = \phi$  and the terms  $\exp [im(\phi - \phi')]$  reduce to one. The electronic density is a function of the radial distance from the interface and is independent of the angular variable.

#### 4. Effect of curvature on solute/interface binding energy

**4.1. Numerical results.** The solute/interface binding energy given by equation (6) is proportional to the electronic density near the interface. The radial electronic density function is:

$$n_o(r) = -\frac{2}{\pi} \int_0^{E_F} dE \sum_{m=-\infty}^{+\infty} \text{Im}g_m(r, r), \quad (19)$$

where  $\text{Im}g_m(r, r)$  is given by equation (18).

The electronic contribution to the point defect energy near the curved interface is obtained by inserting equation (19) into equation (6). We consider only the contribution of electrons with  $k_z = 0$ , thus assuming that the electrons do not propagate along the cylinder axis. Furthermore, we take the constant potential,  $E_m$ , in the metal as the origin of the energies, simplifying the parameter,  $k$ , to  $\sqrt{E/B}$ . We calculate numerically the variation of the electronic energy from the interface in the case of an aluminium matrix ( $k_F = 1.75 \text{ \AA}^{-1}$ ). The energy is computed for a variety of radii of curvature,  $R$ , in the range 1–50  $\text{\AA}$ . The summation over  $m$  is carried out up to  $m = 200$  insuring convergence for all values of  $kR$  and  $kr$  considered. The results for the radial variation of the energy of the point defect are reported in Figure 1. We first note that as  $R$  increases, the energy converges to the limit of the energy of a point defect near a planar interface. As the radius of curvature of the interface decreases, the driving

force for segregation,  $-(\partial\varepsilon/\partial r)$ , increases, indicating segregation enhancement to highly curved interfaces. Away from the interface, the electronic energy of the point defect exhibits Friedel type oscillations. These oscillations offer energy barriers for point defects to overcome during segregation. Due to these oscillations, the electronic energy will only give rise to a very short range driving force for segregation. However, one notes that as the radius of curvature of the interface decreases, the amplitude of the energy oscillations decreases significantly. The attenuation of the amplitude of the oscillations suggests the possibility of longer range segregation to highly curved interfaces.

**4.2. Scaling of binding energy with the radius of curvature.** An expression for the electronic density cannot be obtained analytically. However, in order to obtain an analytical expression for the scaling of the binding energy with the radius of curvature of the interface, we now consider the case of a solute atom located in the neighborhood of the interface. That is, we choose  $r = r_0 = R + \delta r$ . With this choice we can use a Taylor expansion to express the Bessel functions in  $r$  to first order:

$$\begin{cases} J_m(kr) = J_m(kR) + J'_m(kR)k\delta r + \dots \\ Y_m(kr) = Y_m(kR) + Y'_m(kR)k\delta r + \dots \end{cases} \quad (20)$$

We make use of the well known relations for the derivatives of Bessel functions:

$$\begin{cases} J'_m(x) = -J_{m+1}(x) + \frac{m}{x}J_m(x) \\ Y'_m(x) = -Y_{m+1}(x) + \frac{m}{x}Y_m(x) \end{cases} \quad (21)$$

as well as:

$$J_{m+1}(x)Y_m(x) - J_m(x)Y_{m+1}(x) = \frac{2}{\pi x}. \quad (22)$$

After some algebraic manipulations we obtain:

$$\text{Im}g_m(r, r) \cong -\frac{\pi}{2B} \left\{ \frac{4(\delta r)^2}{\pi^2 R^2 [J_m^2(kR) + Y_m^2(kR)]} \right\}. \quad (23)$$

We can now rewrite equation (19) in the form:

$$n_o(r) = \frac{8(\delta r)^2}{\pi^2 R^2} \int_0^{k_F} k dk S(kR), \quad (24)$$

where  $S(kR)$  stands for the summation:

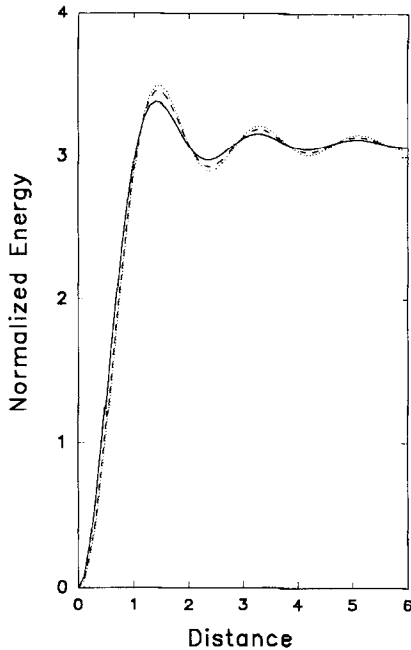
$$S(kR) = \sum_{m=-\infty}^{+\infty} \frac{1}{J_m^2(kR) + Y_m^2(kR)}. \quad (25)$$

$k_F$  in equation (24) is the modulus of the Fermi wave vector.

Making use of the fact that  $J_m^2 = J_{-m}^2$  and  $Y_m^2 = Y_{-m}^2$  the sum,  $S$ , is rewritten in the form:

$$S(kR) = \frac{1}{J_0^2(kR) + Y_0^2(kR)} + 2 \sum_{m=1}^{+\infty} \frac{1}{J_m^2(kR) + Y_m^2(kR)}. \quad (26)$$

We calculate this sum numerically in the case of an aluminum matrix. We also consider a maximum radius of curvature of 400  $\text{\AA}$ .



**Figure 1.** Radial variation of the electronic contribution to a point defect energy near curved interfaces for different radii of curvature of the interface. The normalized energy  $\varepsilon/A$  (in arbitrary units) is plotted as a function of the distance (in  $\text{\AA}$ ) between the point defect and the curved interface [see text and equation (6) for details] ( $R = 1 \text{ \AA}$ : solid line;  $R = 5 \text{ \AA}$ : long dash;  $R = 50 \text{ \AA}$ : dots).

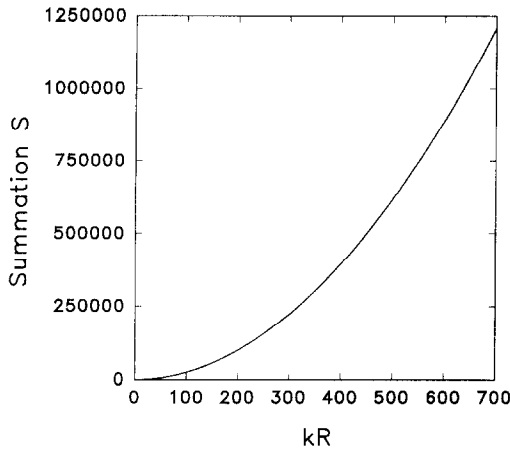


Figure 2. Variation of the summation  $S$  with  $kR$  [see text and equation (26) for details]. The quantity  $kR$  is dimensionless.

The summation is truncated at a maximum value for  $m$  of 1000. This high value insures that the summation converges for all  $kR$  in the interval  $[0,700]$ . We report in Figure 2 the results of this calculation. For large  $kR$ , the summation is a quadratic function of  $kR$  which takes the form  $S(kR) = 2.47 (kR)^2$ . This result implies that for large  $R$ , the energy of the point defect located in the vicinity of the curved interface is independent of the radius. This energy converges toward the energy of a point defect near a planar interface. In the limit of small  $kR$ ,  $S$  varies nearly linearly with  $kR$ . In this limit, equation (24) predicts a point defect energy varying as the inverse of the radius of curvature of the interface.

To elucidate the complete variation of the defect energy with the radius, equation (24) is rewritten in the form :

$$n_o(r) = \frac{8(\delta r)^2}{\pi^2} f(R),$$

where

$$f(R) = \frac{1}{R^4} \int_0^{k_F R} duuS(u). \tag{27}$$

The integral  $f(R)$  is evaluated numerically using the data of Figure 2 and is reported in Figure 3. The transition between small

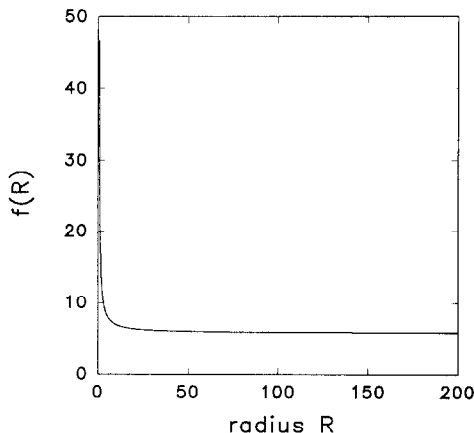


Figure 3. Variation of the function  $f$  with the radius of curvature of the interface [see text and equation (27) for details].

and large values of the radius takes place near  $25 \text{ \AA}$ . For  $R$  larger than  $25 \text{ \AA}$ , the defect energy remains approximately constant as predicted. Below  $25 \text{ \AA}$ ,  $f(R)$  rises drastically, indicating segregation enhancement. The typical radius of fibers used in metal-matrix composites is much larger than this  $25 \text{ \AA}$  limit. Segregation to a metal/insulator interface will not be enhanced by the overall curvature of the fiber. However, irregularities along the fiber such as grooves or corners between facets, for example, those in silicon nitride whiskers, may exhibit local radii of curvature of the order of and even smaller than  $25 \text{ \AA}$ . These irregularities will then augment the driving force for segregation in their vicinity.

In summary, for small arguments,  $kR$ , the sum,  $S$ , varies as the argument itself. The electronic density in the vicinity of the curved interface between the metal and the insulator given by equations (23) and (19) scales as the inverse of the radius of the interface. The binding energy of a solute atom to the interface varies with  $R$  in the same way. This result suggests that the driving force for segregation to curved interfaces is stronger than that for segregation to planar interfaces. It also indicates that solute enrichment near interfaces increases as the radius of curvature decreases.

### 5. Conclusions

We have derived an expression for the electronic contribution to the binding energy of a solute atom near a curved interface between a metal and an insulator. Note, however, that this relation is only valid for the case of a convex metallic interface. To calculate the binding energy near a concave interface, one could consider the case of a cylindrical metallic inclusion embedded in an insulating matrix. In this case, the imaginary part of the Green's function inside the metal vanishes as the electronic states inside the cylinder are quantized. A different approach would then be necessary to evaluate the electronic density near the concave interface. This could be accomplished by using wave functions instead of Green's function and will form the object of another publication. Application of the Green's function method to curved metal/metal interfaces such as curved grain boundaries would require the conservation of the interface response function,  $g(MM)$ , in equation (7) as this term does not vanish in this case. However, difficulties will be encountered from the fact that electronic states will be quantized in the metallic cylindrical fiber.

The electronic energy of a point defect near interfaces with various radii of curvature is calculated numerically. The driving force for segregation increases significantly for small radii of curvature compared to larger ones. The amplitude of energy oscillations away from the interface is attenuated by small radii of curvature allowing longer range segregation effects toward such interfaces. Another key result of this work is that in the limit of small radius of curvature, the electronic contribution to the solute/interface binding energy varies as the inverse of the radius of curvature. The electronic energy is all but one contribution to the driving force for interfacial segregation. An elastic contribution to a solute/curved-interface binding energy can be calculated using Green's functions and the interface response theory in a manner similar to that reported earlier in the case of a planar interface<sup>3</sup>. The dependence on curvature of the elastic contribution to the solute energy can be obtained from simple arguments. The pressure difference,  $\Delta P$ , across a curved surface for instance is inversely proportional to the radius of curvature. The work required for the formation of a point defect with excess volume  $\Delta V$  is to first order  $\Delta P \Delta V$ , leading to an inverse

relationship with the radius of curvature. As the sum of the electronic and elastic energies, the total solute/interface binding energy should also vary as the inverse of the radius of curvature of the interface. The electronic driving force for segregation is shorter range than the elastic contribution due to Friedel type oscillations in the point defect/interface electronic energy. The electronic energy will play a dominant role on segregation in the very near vicinity of the interface. The electronic contribution to segregation will be even more important for metal matrices and insulator fibers with similar elastic moduli as the elastic driving force for segregation vanishes in the limit of media with identical elastic properties<sup>5</sup>.

In conclusion, we have shown in this work that segregation

should be significantly affected by interfacial morphology and that solute enrichment should be more important near highly curved interfaces than near planar interfaces.

#### References

- <sup>1</sup> J M Briceno-Valero, Morphology of grain boundary segregation : effect on grain boundary structure in Al-Zn alloys. D o E Report, LBL-13626, p. 30 (1981).
- <sup>2</sup> G Allan, *Annal Phys*, **5**, 169 (1970).
- <sup>3</sup> L Dobrzynski, *Surf Sci*, **180**, 489 (1987).
- <sup>4</sup> P M Morse and H Feshbach, *Methods of Theoretical Physics, Vol I*, p. 827. McGraw-Hill, New York (1953).
- <sup>5</sup> J O Vasseur, P A Deymier, B Djafari-Rouhani and L Dobrzynski, *Interface Sci*, **1**, 49 (1993).