Driving force for the electromigration of a substitutional impurity

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Using the relation between the effective valence and the charge flux associated with a unit flux of a solute atom, we calculate the effective valence for the electromigration of a substitutional impurity. The formula for the force on an impurity near its stable position is compared with that obtained in previous calculations.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as I) we show that the driving force for the electromigration of an impurity in a homogeneous medium is related to the net flux of charge induced by the displacement of the impurity, in a system free of external fields. Although this relation follows from general thermodynamic considerations,[2] the microscopic calculation of I identifies precisely the different contributions to the force acting on the impurity. The friction force on the impurity is related to the opposite of the force exerted by the impurity on the electron gas, an approximation which is reasonable for an isolated impurity in a liquid metal for instance. This approximation remains valid for an interstitial impurity completely decoupled from the lattice, if it is assumed that the electronic structure of the impurity does not change during the diffusion jump.

The present paper is devoted to the analysis of the force for the electromigration of a substitutional impurity in a solid solution. The calculation of the force on the impurity is complicated by the fact that, when a substitutional impurity is displaced from its stable position, two interacting defects appear: the impurity ion itself and the vacancy it leaves at its initial site. Throughout this paper we ignore the presence of the vacancy neighboring the substitutional impurity and we address to the problem of calculating the force on the substitutional ion near its stable position. In particular, we show that if the force on the impurity is identified with the opposite of the force on the electron gas due to the presence of the impurity, the usual Bosvieux-Friedel[3,4] formula is recovered. We also show that the effective valence of the impurity is related to the charge flow induced by the displacement of the impurity alone. As a vacancy is left behind the moving impurity, the result obtained for the force is not given by the Bosvieux-Friedel formula. In Sec. II we calculate explicitly this force and interpret the results in terms of the polarization charge of the ion-vacancy complex.

II. EFFECTIVE VALENCE OF A SUBSTITUTIONAL IMPURITY

A. Phenomenological analysis

We consider a substitutional impurity of charge Z' in a crystal, the ions of which have the charge Z. As in I we separate the electrons of the system in two classes, in the jellium approximation: (i) a uniform electron density $n_0 = Z/\Omega$, where Ω is the atomic volume of the perfect crystal; (ii) the n_i $(Z'-Z)$ electrons of the screening clouds of the n_i impurities per unit volume.

In an electric field $\vec{E}$, these electrons experience the electrostatic force $-n_i (Z'-Z)|e|\vec{E}$, an elastic force f_1 from the impurity ions and a friction force g from the conduction electrons. The mechanical equilibrium of the electrons in the screening clouds requires that

$$-n_i (Z'-Z)|e|E + f_1 + g = 0. \tag{1}$$

On the other hand, the friction force experienced by the conduction electrons, due to the presence of the impurities, is

$$F_f = -g + f_2, \tag{2}$$

where f_2 is the force applied by the bare impurity ions on the conduction electrons. This friction force F_f on the electron gas accounts for the residual resistivity ρ_i of the impurity. As the net friction force on the electron gas is $n_0|e|E$ per unit volume, we find, using the Matthiessen approximation,

$$F_f/n_0|e|E = \rho_i n_i/\rho, \tag{3}$$

where $\rho = \rho_0 + \rho_i n_i$ is the resistivity of the solid solution. Combining (1)–(3) we find the force on one impurity

$$F = Z'|e|E - (f_1+f_2)/n_i$$
$$= [Z - (\rho_i/\rho)n_0]|e|E, \tag{4}$$

leading to the effective valence

$$Z^* = Z - n_0\rho_i/\rho. \tag{5}$$

As we shall show now, this force F can be con-

sidered as acting on a complex made of the ion of charge Z' itself and the vacancy it leaves behind it. Therefore the net force acting actually on the moving ion is only a part of F which we calculate now.

B. Microscopic derivation of the force on a substitutional impurity near its stable position

We consider a unit volume of the crystal containing one substitutional impurity. We assume that this impurity is slowly moving at the constant velocity $\vec{u} = d\vec{R}/dt$ along the z direction, with respect to the lattice, and we consider only very small displacements around the equilibrium position $\vec{R}_1$ of the impurity:

$$\vec{R}(t) = \vec{R}_1 + \vec{u}\,t \ . \tag{6}$$

The Hamiltonian of the system of $n_0 + (Z' - Z)$ electrons can be written

$$H(t) = H_0 - V_0(\vec{R}_1) + V_1(\vec{R}(t))$$
$$= H_1 + V_1(\vec{R}(t)) \ , \tag{7}$$

where H_0 includes the kinetic energy of the electron gas as well as electron-phonon and electron-electron interactions; V_0 and V_1 are the bare interaction potentials of the electrons with a solvent and the solute ion, respectively,

$$V_0(\vec{R}_1) = -\sum_l \frac{Z e^2}{|\vec{r}_l - \vec{R}_1|} \ ,$$
$$V_1(\vec{R}(t)) = -\sum_l \frac{Z' e^2}{|\vec{r}_l - \vec{R}(t)|} \ , \tag{8}$$

where $\vec{r}_l$ denotes the position of the lth electron.

As we consider only small displacements around the site $\vec{R}_1$, $H(t)$ can be expanded up to first order in ut:

$$H(t) = H_0 - \sum_l \frac{(Z' - Z) e^2}{|\vec{r}_l - \vec{R}_1|} + ut \left(\frac{\partial V_1}{\partial z}\right)_{\vec{R}_1} . \tag{9}$$

(a) We calculate now the electron flux J_e induced by the displacement of the impurity in a sample free of external fields. As in I we can write

$$J_e = \sum_{mn} \delta\rho_{mn} \dot{Z}_{nm} \ , \tag{10}$$

where

$$\dot{Z} = \sum_l \dot{z}_l$$

is the z component of the velocity operator of the electron gas; $\delta\rho(t)$ is the departure of the electron density matrix from the value $\rho_0(t)$ it would have if the reaction of the electron gas to the impurity displacement were instantaneous:

$$\rho_0(t) = e^{-\beta H(t)}/\mathrm{Tr}(e^{-\beta H(t)}) \ . \tag{11}$$

It can be shown that, to first order in ut, $\delta\rho(t)$ is the solution of the linearized[5] Liouville Eq. (1):

$$i\,\frac{d\rho_0(t)}{dt} = [H(t), \delta\rho(t)] - i\eta\,\delta\rho(t) \quad (\eta = 0^+) \ , \tag{12}$$

so that the ratio of the net electron flux to the impurity velocity u is

$$\left(\frac{J_e}{u}\right)_{E=0} = -\sum_{mn} \frac{\nu_m - \nu_n}{E_m - E_n - i\eta} F_{mn} Z_{nm} \tag{13}$$

when the impurity crosses its stable position. In Eq. (13) ν_m is the occupation number of the mth eigenstate of $H(0)$:

$$\nu_m = \langle m | \rho_0(0) | m \rangle$$

and E_m is the corresponding energy eigenvalue. F_{mn} is the matrix element of the z component of the force operator

$$F = -\frac{\partial V_1}{\partial z} \ . \tag{14}$$

(b) We consider now that the sample is submitted to an external electric field $\vec{E}$. The force on the impurity located at the site $\vec{R}_1$ is

$$\vec{F}_s = Z' | e| \vec{E} + \langle \vec{F} \rangle = Z_s^* | e| \vec{E} \ . \tag{15}$$

In this expression, the first term is the electrostatic force on the impurity ion and $\langle \vec{F} \rangle$ denotes the force on the impurity, due to electron-impurity interactions.

Using standard linear response theory as in I, we obtain

$$\langle \vec{F} \rangle = \sum_{mn} \frac{\nu_m - \nu_n}{E_m - E_n + i\eta} F_{mn} Z_{nm} | e| \vec{E} \ . \tag{16}$$

On comparing (13), (15), and (16), we show that the effective valence Z_s^* of the substitutional impurity sitting on its stable position is

$$Z_s^* = Z' - (J_e/u)_{\vec{E}=0} \ . \tag{17}$$

Equation (17) is quite general and can be demonstrated from thermodynamic considerations: $Z_s^* u$ is the flux of electric charge associated with the displacement of the impurity ion of velocity u.

(c) In order to calculate $(J_e/u)_{\vec{E}=0}$, we notice that the Hamiltonian (9) can be written

$$H(x, y, t) = H_0 - x \sum_l \frac{e^2}{|\vec{r}_l - \vec{R}_1|}$$
$$- y \frac{\partial}{\partial z} \left(\sum_l \frac{e^2}{|\vec{r}_l - \vec{R}(t)|}\right)_{t=0} ut \ , \tag{18}$$

and the expression (7) is recovered when $x = Z' - Z$ and $y = Z'$.

Using this two-parameter Hamiltonian, we can write

$$(J_e/u)_{\vec{E}=0} = K(x,y)$$

$$= f(x) + yg(x) + y^2 h(x) + \cdots , \qquad (19)$$

and we determine now the functions f, g, and h.

When $y = 0$, no current can take place in the system, so that $f = 0$. When $x = 0$ and $y = Z$, the Hamiltonian (18) refers to a perfect crystal with a moving ion close to the site $\vec{R}_1$. As there is no friction force on an ion of the host metal at its stable position, the only contribution to J_e is the convective flux Zu due to the displacement of its screening charge Z and

$$K(0,Z) = Zg(0) + Z^2 h(0) + \cdots = Z , \qquad (20)$$

so that $h(0) = 0$.

Keeping only terms up to the second order in x and y in the development (19) we obtain

$$K(x,y) = yg(x) . \qquad (21)$$

Considering now the case where $x = y = Z'$, the Hamiltonian (18) describes an interstitial of charge Z' at site $\vec{R}_1 + \vec{u}t$ in an otherwise perfect crystal and, from [I, Eq. (46)]

$$Z'g(Z') = Z' + n_0 \rho_i(Z')/\rho , \qquad (22)$$

where $\rho_i(Z')$ is the specific resistivity of an interstitial of valence Z' and ρ is the resistivity of the alloy. Then

$$g(x) = 1 + n_0 \rho_i(x)/\rho x$$

and

$$(J_e/u)_{\vec{E}=0} = y[1 + n_0 \rho_i(x)/\rho x] . \qquad (23)$$

In particular, in the substitutional case $(x = Z' - Z ; y = Z')$

$$(J_e/u)_{\vec{E}=0} = Z' + n_0[Z'/(Z'-Z)]\rho_i(Z'-Z)/\rho \qquad (24)$$

and

$$Z_s^* = -n_0[Z'/(Z'-Z)]\rho_i(Z'-Z)/\rho . \qquad (25)$$

III. DISCUSSION

Equation (25) shows that, like in the interstitial case, there is no direct electrostatic force on the impurity, on account of the cancellation between the forces on the ion and on the electrons of the screening cloud.

This result is contrary—even in the simple case of an interstitial—to those obtained in a number of calculations,[6-9] working from different approaches and approximations. The fact that the electrostatic force vanishes rests on the division of the electrons in two categories namely those which conduct and those which shield the impurity ion. As the screening charge is localized around an impurity (substitutional or interstitial) or a va-

cancy, we feel that this division is physically possible. In our treatment, the electrostatic force is related to the electrostatic charge carried out by the impurity when it is moved in a sample free of external fields (excluding the scattering current). When an impurity (interstitial or substitutional) is made to cross an imaginary plane P in the system, observation of the initial and final states shows that the total electrostatic charge of the two regions defined by P has not changed: (i) In case of an interstitial impurity, the total electrostatic charge of the defect is $Z' + (-Z') = 0$; then a net charge zero crosses the plane P. (ii) In an interchange of a substitutional impurity with a vacancy, the net charge of the screened impurity $[Z' - (Z' - Z) = Z]$ and the net charge of the vacancy $[0 - (-Z) = Z]$ are exchanged and the net charge crossing P is again zero.

These considerations rely on the hypothesis of complete and instantaneous screening of the defects during the diffusion jump. This approximation is acceptable in normal or noble metals for which the order of magnitude of the screening time is of the order of ω_p^{-1}, the inverse of the plasma frequency, what is much smaller than the jump time. In transition metals where the screening takes place in the d band, or in semiconductors, this may not be the case, as shown for instance in the experiments of Erckman and Wipf.[10]

The effective valence Z_s^* involves the resistivity of the solute and the corrective factor $Z'/(Z'-Z)$ which can be explained as follows: (a) The friction force experienced by the electron gas, due to the presence of the impurity, is proportional to $\rho_i(Z' - Z)$ when the impurity is close to its stable position. (b) When the impurity is slightly displaced from this position, the defect is actually dissociated in a vacancy and an "interstitial" of charge Z' carrying a screening cloud of Z' electrons. Therefore the net force on the dissociated defect can be split into two parts: a force on the very impurity, proportional to $-Z'\rho_i/(Z' - Z)$ or to $-Z'(Z' - Z)$ in the Born approximation, and a force on the vacancy, proportional to $[Z/(Z' - Z)]\rho_i$. This can be understood in the framework of the theory of Bosvieux and Friedel: the force on the impurity, proportional to $Z'(Z' - Z)$ can be viewed as the force experienced by the bare charge Z' in the polarization field created by the screening cloud of the impurity-vacancy complex containing $Z' - Z$ electrons. This point of view is also implicit in the work of Sorbello.[4]

The effective valence for electromigration can be obtained by averaging the force acting on the impurity, along its diffusion path. Assuming that the impurity behaves as an interstitial of charge Z' at the saddle point, we obtain for the effective

valence of the impurity

$$Z_i^* = -\tfrac{1}{2}(n_0/\rho)\{[Z'/(Z'-Z)]\rho_i(Z'-Z)+\rho_i(Z')\}.$$

(26)

Similarly the effective valence of a solvent atom is

$$Z_0^* = -\tfrac{1}{2}(n_0/\rho)\rho_i(Z)$$

(27)

as it may be considered as an interstitial of charge Z when it crosses the saddle point. The effective valence of the solute i with respect to the solvent is therefore

$$Z_i^* - Z_0^* = -\tfrac{1}{2}(n_0/\rho)\{[Z'/(Z'-Z)]\rho_i(Z'-Z)$$
$$+\rho_i(Z') - \rho_i(Z)\}.$$

(28)

This formula is strictly valid for dilute solutions, as we consider that the alloy resistivity ρ does not change during the diffusion jump. For a practical use of (28) it is possible to identify the specific resistivity $\rho_i(x)$ with that of the impurity of valence $Z+x$ in the metal of valence Z, as suggested in Ref. 11. For instance the effective valence of Cd in Ag involves $\rho_i(Z'-Z)=\rho_i(1)$ (resistivity of Cd in Ag); $\rho_i(Z')=\rho_i(2)$ (resistivity of In in Ag); $\rho_i(Z)=\rho_i(1)$ (Cd in Ag).

In the framework of the Born approximation, $\rho_i(x)\sim x^2$ and we obtain

$$Z_i^* - Z_0^* \sim z(z+\tfrac{3}{2}Z),$$

(29)

where $z=Z'-Z$, instead of

$$Z_i^* - Z_0^* \sim z(z+Z)$$

(30)

as derived by Doan,[12] using the model of Bosvieux and Friedel. In monovalent metals, these two formulas agree reasonably well with the experimental data of Doan[12] in Ag and of Turban[13] and Guilmin et al.[14] in Cu.

There is a striking difference however between our model and that of Doan when one calculates the resistivity $\rho_i(\text{sp})$ at the saddle point from the measured value of $Z_i^* - Z_0^*$.

We define the resistivity $\overline{\rho_i}$ involved in the formula giving the mean force on the moving ion by

$$2\overline{\rho_i} = [Z'(Z'-Z)]\rho_i(Z'-Z)+\rho_i(\text{sp}).$$

(31)

In the analysis leading to (28) we assumed that $\rho_i(\text{sp})=\rho_i(Z')$. Another way of using Eq. (28) is to estimate the value of the saddle-point resistivity $\rho_i(\text{sp})$ from the measured value of $Z_i^* - Z_0^*$. The difference between the values $\rho_i'(\text{sp})$ and $\rho_i''(\text{sp})$ obtained for this saddle-point resistivity when use is made of our model or that of Doan is

$$\rho_i'(\text{sp}) - \rho_i''(\text{sp}) = [Z/(Z'-Z)]\rho_i(Z'-Z),$$

(32)

which is positive or negative according to the sign of $Z'-Z$.

This observation could account for the fact that saddle-point resistivities of impurities in monovalent metals are often found too small when use is made of the formula given by Doan. On the other hand, the difference (32) should be particularly large in polyvalent metals, like aluminum. In particular, the experimental data obtained by Limoge[15,16] should be analyzed along these lines. It is very difficult however to get a quantitative estimation of $\rho_i(\text{sp})$ as a lot of approximations are made to obtain a formula like (31):

(i) The apparent effective valence of the solute must be corrected for the vacancy wind effect, which is unfortunately very difficult to estimate.

(ii) The effect of the relaxations around the impurity is not considered explicitly. In particular $\rho_i(Z'-Z)$ is generally identified with the impurity resistivity ρ_i^L measured by Linde. This is an approximation as the force on the impurity involves only the scattering of electrons on the impurity itself whereas ρ_i^L involves the electron scattering on the neighboring relaxed ions as well.

(iii) The diffusion jump involves point defects in strong electronic and elastic interaction, and it is difficult to identify the contribution of each defect to the force on the electron gas. A complete dynamical analysis of the jump process should be performed to identify each contribution and to get an effective driving force for the electromigration process.

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