

Point defects and inclusions near solid surfaces and interfaces (*)

B. MICHEL (HALLE)

THE PAPER is concerned with the influence of solid surfaces and interfaces on the elastic energy of point defects and inclusions. The reactions between point defects and volume defects in solids are governed by diffusion-controlled processes, the diffusion current being strongly affected by the elastic potential gradient field $\text{grad } E$ around the defects. Basing upon continuum mechanics, the calculation of E is possible; the results are presented in this paper. Some new aspects of application in solid state physics and physical chemistry are discussed.

Rozpatruje się wpływ powierzchni ciał stałych i powierzchni styku ciał stałych na energię sprężystą defektów punktowych i domieszek. Reakcje pomiędzy defektami punktowymi w ciałach stałych rządzone są przez procesy kontrolowane przez dyfuzję, ponieważ prąd dyfuzji pozostaje pod silnym wpływem gradientu sprężystego pola potencjalnego ($\text{grad } E$) wokół defektów. Podaje się rezultaty obliczenia E na podstawie zasad mechaniki ośrodków ciągłych. Przedyskutowano pewne nowe aspekty zastosowań rozważanych zależności w fizyce ciała stałego i w chemii fizycznej.

Рассматривается влияние поверхности твердых тел и поверхности контакта твердых тел на упругую энергию точечных дефектов и примесей. Реакции между точечными дефектами в твердых телах описываются процессами контролируемые диффузией, т. к. ток диффузии остается под сильным влиянием градиента потенциального упругого поля ($\text{grad } E$) вокруг дефектов. Приведены результаты расчета E , опираясь на принципы механики сплошных сред. Обсуждены некоторые новые аспекты применений рассматриваемых зависимостей в физике твердого тела и в физической химии.

1. Introduction

IT IS A WELL-KNOWN fact that the majority of reactions between point defects in solids can be considered to be diffusion-controlled [1]. Diffusion of point defects has become the subject of many investigations [2, 3]. In recent years, there has been a growing interest in the diffusion equation for point defects including the elastic drift term due to the elastic interaction between the defects [4, 3].

Diffusing self-interstitials have been found to become trapped at impurity atoms within certain temperature regions [5]. A rough estimation already shows that the elastic energy of an interstitial in the strain field of an impurity comes into the order of magnitude of the thermal energy [6]. Coulomb interaction can be neglected when compared with the elastic interaction at least for distances larger than one lattice parameter [7, 4]. The phenomenological description of the drift diffusion yields essentially the same results as the lattice theory does if the source of migrating defects is not close to the trapping sites [4].

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2. Stress assisted diffusion of point defects

The diffusion equation for point defects of concentration c in the presence of an elastic potential gradient field E is given by the relation

$$(2.1) \quad \frac{\partial c}{\partial t} = \nabla \cdot \left(D \nabla c + \frac{Dc}{kT} \nabla E \right),$$

D being the diffusion coefficient, k the Boltzmann constant, and T the temperature [8, 9]. SEEGER [9] showed that for the steady-state case the first-order gradient term can be avoided. This leads to a Schrödinger equation:

$$(2.2) \quad \Delta \psi + U_1 \psi = 0,$$

where ψ is related to the concentration c by

$$(2.3) \quad \psi = c \exp \left(\frac{E}{2kT} \right)$$

and

$$(2.4) \quad U_1 = \frac{\Delta E}{2kT} - \left(\frac{\nabla E}{2kT} \right)^2.$$

Equation (2.2) is important for describing the segregation processes of solute atoms and the formation of oxide layers. Experiments on the interaction-induced defects with impurities have also pointed at the great importance of the elastic interaction potentials for the phenomenon of stress-assisted drift diffusion in solids [3, 4]. The well-known theory of spinodal decomposition developed by CAHN [10], which has been further improved and applied by FILIPOVICH, DMITRIEV [11] and others, also manifests the great importance of the elastic energy of a defected region in a solid [13, 14].

The aim of the present paper is to deal with the elastic interaction between point defects and more or less extended inclusions ("volume" defects) under the immediate influence of the solid surface and an interface, grain boundary surface etc.

3. Influence of surfaces and interfaces on the elastic interaction energy of defects

A dilatation centre in an isotropic body can interact with hydrostatic stress only. Hence it follows that interaction between two dilatation centres exists only in finite bodies [15, 16]. The theory of elasticity provides a convenient framework for calculating the internal stress and strain field associated with point defects and volume defects in solids [17–22]. Moreover, it has long been known that a free surface, a surface layer or an interface attract or repel defects. In 1972 BACON first gave an exact solution for the interaction energy of a dilatation centre with a surface layer of arbitrary thickness applying Hankel transforms [21]. WOLFER and MANSUR [22] investigated the same type of defects near a spherical surface layer. By comparing this results with those already known from literature, Bacon showed that the latter (ESHELBY [23], BULOUGH, LOVE and others [21]) had been approximations only. This was confirmed by the investigations of the authors [24,

30, 32]. We have generalized some formulae of Bacon's paper taking into consideration the shape and the size of the defects, the modulus effect between defects and matrix being neglected.

If we discuss the defect configuration shown in Fig. 1 for the case of a so-called "internal" interface ($d \rightarrow \infty$, the surface is far remote from the interface $z = 0$), we arrive

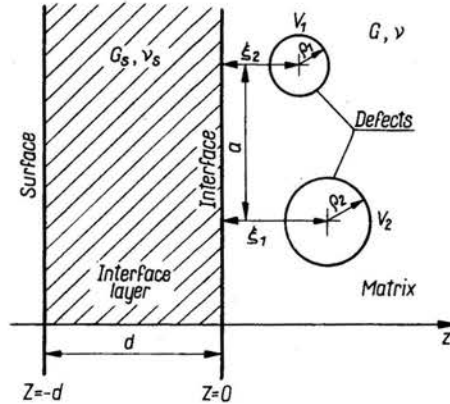


FIG. 1.

at the problem of defects in coupled semi-spaces. The problem (in the static case) is not difficult and can be solved using the theory of elasticity. If the defects with the volumes V_1 and V_2 are characterized by their relative "quasi-plastic" volume dilatations (first stress-free strain invariant) $\delta\eta_1$ and $\delta\eta_2$ with respect to the matrix [24], the elastic interaction energy between V_1 and V_2 is given by the following expression [25]:

$$(3.1) \quad E_{\text{int}}^{(2)} = \frac{G(\gamma-1)(1+\nu)^2}{9\pi(1-\nu)[1+\gamma(3-4\nu)]} \left\{ \int \int \int_{V_1} \delta\eta_1 \frac{\partial^2 \Phi_2}{\partial z^2} dV + \int \int \int_{V_2} \delta\eta_2 \frac{\partial^2 \Phi_1}{\partial z^2} dV \right\},$$

where $\gamma = G_s/G$ denotes the ratio of the shear moduli of interface layer and matrix, respectively, ν is the Poisson ratio of the matrix. $\delta\eta_i$ can be an arbitrary function of position inside the defects V_i . The influence of $\delta\eta_i$ on the strain energy of a spheroidal defect was discussed by LOGES [12]. The formula (3.1) follows from the theory of elasticity [25] taking into account the well-known fact that the mean value of the trace of the stress tensor vanishes:

$$(3.2) \quad \int \int \int_{V_{\text{tot}}} \sigma_{ii} dV = 0,$$

the integral being taken over the whole solid which is not acted upon by additional external tractions. Equation (3.2) was derived by NOWACKI [26] and HIEKE [27]

Equation (3.1) is a generalization of a previous formula of the author concerning only the interaction energy of such kinds of defects where $\delta\eta_i$ was held constant [24]. Φ_1 and Φ_2 are the "image" potential functions

$$(3.3) \quad \Phi_i(P) = \int \int \int_{V_i} \delta\eta_i(P_i) R(P_i P) dV(P_i),$$

with the kernel functions

$$(3.4) \quad R(P, P_i) = [(x-x_i)^2 + (y-y_i)^2 + (z+z_i)^2]^{-1/2}.$$

for the interaction energy $E_{\text{int}}^{(1)}$ of one defect with the interface the expression

$$(3.5) \quad E_{\text{int}}^{(1)} = \frac{(\gamma-1)(1+\nu)^2 G}{9\pi(1-\nu)[1+\gamma(3-4\nu)]} \int \int \int_{V_i} \delta\eta_i \frac{\partial^2 \Phi_i}{\partial z^2} dV$$

is obtained. Equation (3.5) is a generalization of a formula given by BACON [21].

The influence of a free solid surface on the defect is described by the condition $\gamma = 0$. This yields

$$(3.6) \quad E_{\text{int}}^{(1)} = -\frac{(1+\nu)^2 G}{9\pi(1-\nu)} \int \int \int_{V_i} \delta\eta_i \frac{\partial^2 \Phi_i}{\partial z^2} dV.$$

The case $\delta\eta_i = \text{constant}$ is investigated in detail in [28–30].

The total elastic energy $E_{\text{tot},i}^{(1)}$ stored in the medium containing one defect is obtained by adding the Crum-Nabarro energy $E_{0,i}$ of the defect V_i in an unbounded isotropic homogeneous matrix

$$(3.7) \quad E_{0,i} = \frac{2G(1+\nu)}{9(1-\nu)} \overline{(\delta\eta_i)^2} V_i.$$

It follows that

$$(3.8) \quad E_{\text{tot},i}^{(1)} = E_{0,i} \left(1 - \frac{1+\nu}{2\pi(\delta\eta_i)^2 V_i} \int \int \int_{V_i} \delta\eta_i \frac{\partial^2 \Phi_i}{\partial z^2} dV \right),$$

the mean square value $\overline{(\delta\eta_i)^2}$ being defined by

$$(3.9) \quad \overline{(\delta\eta_i)^2} = \frac{1}{V_i} \int \int \int_{V_i} (\delta\eta_i)^2 dV.$$

For a spherical defect of the radius ρ_i , and supposing a constant value $\delta\eta_i$, we arrive at the formula

$$(3.10) \quad E_{\text{tot},i}^{(1),s} = E_{0,i} \left(1 - \frac{1+\nu}{6} \frac{\rho_i^3}{\xi_i^3} \right),$$

ξ_i being the distance between the centre of the defect and the surface [21, 32, 33]. An incompressible defect immediately at the boundary surface ($\rho_i = \xi_i$) is connected with a reduction of energy by 25% due to the influence of the surface. JÄGER compared the expression (3.10) with the results obtained by the lattice theory and found a good agreement [33]. The influence of an interface upon two spherical volume defects (or point defects) was investigated by the author [28]. This yields

$$(3.11) \quad E_{\text{int}}^{(2)} = \frac{32\pi(\gamma-1)G(1+\nu)^2}{81(1-\nu)[1+\gamma(3-4\nu)]} (\delta\eta_1)(\delta\eta_2)\rho_1^3\rho_2^3(8\xi^2-a^2)(4\xi^2+a^2)^{-5/2},$$

ρ_1 and ρ_2 being the radii of the two defects. ξ denotes the mean distance $\xi = \frac{\xi_1 + \xi_2}{2}$, a is explained in Fig. 1.

For $\gamma = 0$ we obtain the following expressions for the interaction energy of two spherical defects under the influence of a solid surface:

$$(3.12) \quad E_{\text{int}}^{(2),s} = \frac{-32\pi}{81(1-\nu)} (1+\nu)^2 G(\delta\eta_1) (\delta\eta_2) \rho_1^3 \rho_2^3 (8\xi^2 - a^2) (4\xi^2 + a^2)^{-5/2}.$$

A discussion of Eq. (3.12) is found in [30].

Also of interest is the fact that the interface influences the interaction energy of the two defects in such a way that both attraction and repulsion occur, depending both on geometrical and mechanical parameters. A hard layer ($\gamma > 1$) leads to a repulsion force between the defects if the distance between them is small enough. Attraction occurs if the defects are very remote from each other. In contrary, two defects of equal kind near a free surface [28] repel if their distance is great. If the distance tends to zero, there exists a bound state. A comparison of the results with those obtained for the interaction energy in the unbounded anisotropic medium leads to the assertion that a solid surface acts on the defects like a crystal anisotropy [30].

The model presented in this paper has been investigated in detail for many special cases of the defect anisotropy. For spheroidal defects, for instance, the integration of Eqs. (3.1) and (3.5) was carried out and suitable approximation formulae were established. It is also possible to take into account the additional influence of a finite thickness d of the surface layer or interface layer [25].

If the condition

$$(3.13) \quad d \gg \sqrt[3]{V_i}$$

is satisfied, for defects near the interface at $z = 0$ (see Fig. 1) the following approximation formula can be derived:

$$(3.14) \quad E_{\text{int}}^{(1)} = - \frac{4G(1+\nu)^2}{9\pi[1+\gamma(3-4\nu)]} \int \int \int_{V_i} \left\{ \frac{1-\gamma}{4(1-\nu)} \delta\eta_i \frac{\partial^2 \Phi_i}{\partial z^2} + \gamma \delta\eta_i \frac{\partial^2 \psi_i}{\partial z^2} \right\} dV,$$

where ψ_i is given by

$$(3.15) \quad \psi_i(P) = \int \int \int_{V_i} T(P_1 P_i) \delta\eta_i(P_i) dV(P_i),$$

with the kernel function

$$(3.16) \quad T(P, P_i) = [(x-x_i)^2 + (y-y_i)^2 + (z+z_i+2d)^2]^{-1/2}.$$

The formula (3.14) can be improved taking into consideration more terms of a perturbation series ("image" terms). From Eq. (3.14) we can draw an interesting conclusion, namely that for $\gamma > 1$ and for constancy of the interaction energy $E_{\text{int}}^{(1)}$ of spherical defects will change its sign if d becomes small enough. This means that surface exerts a predominant influence on the defects if the surface layer is very thin. This conclusion agrees with the results obtained by Bacon for a singular dilatation centre.

For $\delta\eta_i = \text{constant}$ the following criterion can be derived for volume defects near an "internal" interface ($d \rightarrow \infty$):

$$(3.17) \quad E_{\text{int}}^{(1)} \geq 0 \quad \text{if} \quad \gamma \leq 1.$$

From this it follows that a surface of a solid always attracts volume defects of this kind for arbitrary shape and size. For dilatation centres this was already proved by Bacon.

4. Conclusions and remarks

The presented formulae have to be considered as correction terms for the total mechanical energy of the defects (defected regions) near interfaces or free surfaces. These formulae provide the basis for further improvements of the theory of liquation processes and related diffusion phenomena near interfaces, which require improved calculations of the elastic part of free energy [11, 13, 35, 14]. The next step to a more comprehensive model is the additional consideration of the "defect-matrix modulus effect" as it has been done, for instance, by ESHELBY [34] for an inclusion in the bounded medium. From the viewpoint of the solid state physicist, the decisive problem does not consist in solving the boundary value problem numerically, but in deriving suitable analytic expressions (as a rule this means suitable approximations) for the elastic interaction energy. This can be applied for further investigations in different branches of solid state physics and physical chemistry, for instance as drift potentials in Eq. (3.1). A wide application of the energy formulae is due to the dependence of quasi-plastic volume dilatation $\delta\eta_i$ on concentration fluctuations in solids near surfaces and interfaces.

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MARTIN-LUTHER-UNIVERSITÄT, HALLE, DDR.

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