

## PHASE TRANSFORMATIONS

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### Excessive Pressure in the Subsurface Layer in a Crystal

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As shown, the formation of surface of a semi-infinite crystal is accompanied with excessive pressure arising inside the subsurface region, resulting in changes of structural and phase states of this region.

Показано, що утворення поверхні напівнескінченного кристалу супроводжується надлишком тиску в приповерхневій області, що спричиняє зміну її структурного та фазового станів.

Показано, что образование поверхности полубесконечного кристалла сопровождается избыточным давлением в приповерхностной области, что является причиной изменения её структурного и фазового состояний.

**Key words:** surface, phase transformation, pressure effects, Lennard-Jones potential.

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## 1. INTRODUCTION

It is a long-established fact that presence of surface can substantially affect the nature of phase transformations in solids. The most well-known example of such influence is the phenomenon of surface melting, *i.e.* formation of a liquid layer at the crystal surface at temperature lower than the bulk melting point  $T_{mb}$  by several degrees (or several tenths of degrees) [1, 2]. A shift of the order–disorder phase transition is also observed for Cu–Au alloy [3]. For practical applications, formation of nanosize heterostructures on surfaces of semiconductors, such as gallium arsenide, is especially important [4, 5].

In the present study, we show that formation of the surface of a semi-infinite crystal is accompanied with excessive pressure arising in

the subsurface region and affecting both structural and phase state of this region.

## 2. THERMODYNAMIC RELATIONS

In the phase transition curve,  $T_m = T_m(P)$ , the chemical potentials of the phases are equal

$$\mu_1(T_m, P) = \mu_2(T_m, P). \quad (1)$$

Here, indices 1 and 2 denote a one-component low-temperature phase and a high-temperature phase, respectively.

Differentiating (1) with respect to pressure and taking into account  $T_m = T_m(P)$  dependence leads to the Clausius–Clapeyron equation (see, *e.g.*, [6, 7])

$$T_m = T_{mb} + \frac{T_{mb}(v_2 - v_1)}{\lambda} \Delta P, \quad (2)$$

giving a relationship between a change in the phase transition temperature,  $\Delta T = T_m - T_{mb}$ , and a change in pressure in the system,  $\Delta P = P - P_b$ . In Eq. (2),  $\lambda = T(s_2 - s_1)$  is specific heat of formation of a flat subsurface layer of phase 2,  $s_i$  is entropy per atom of phase  $i$ ,  $v_i$  is volume per atom of phase  $i$ . To determine  $\lambda$ , let us proceed from the fact that thermodynamic potentials of phases 1 and 2 are equal when a flat layer of subsurface phase of thickness  $l$  is formed. Hence, we obtain the  $\lambda$  expressed as

$$\lambda = \lambda_0 + \Delta P v_2 + \frac{(\sigma_2 + \sigma_{12} - \sigma_1)}{\rho_2 l}, \quad (3)$$

where  $\lambda_0$  is specific heat (heat per atom) of phase transformation for the bulk phase,  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_{12}$  are specific surface energies of phases 1, 2 and interface 1–2, respectively,  $\rho_2$  is a number of atoms in unit volume of the phase 2. It follows from (2) and (3) that, since  $\rho_2 l S \approx 1$ , a change of the surface energy due to formation of a new phase area slightly affects  $\lambda$  and, therefore, a shift of the phase transition temperature (2).

To determine excessive pressure  $\Delta P$  arising in the subsurface region, let us consider the process of formation of a semi-infinite crystal from the bulk solid phase [8].

Let  $w_0(r_{ij})$  be potential of pairwise interatomic interaction, and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  be distance between the atoms  $i$  and  $j$ . Atom  $i$  of the bulk crystal is in the total potential given by

$$U^0 = U_i = \sum_{j \neq i} w_0(r_{ij}), \quad (4)$$

where  $i > 0$  for atoms of the upper half-space, and  $i \leq 0$  for atoms of the lower half-space.

Formation of a semi-infinite crystal (with the crystal surface being in the plane  $z = 0$ , while the crystal itself being located in the region of  $z \leq 0$ ) is equivalent to superposing an additional atomic potential  $\varphi(z)$  in the subsurface region onto the potential (4). Formally, removing impact of atoms located in the upper half-space  $z > 0$  of the bulk crystal on atoms of the subsurface region of the lower half-space,  $z \leq 0$ , can be represented as superposing a lattice of particles with the interatomic potential  $-w_0(r_{ij}^0)$  onto atoms of the upper half-space. Then an atom of the semi-infinite crystal is in the potential given by

$$U(z_i) = U^0 + \varphi(z_i), \quad (5)$$

where

$$\varphi(z_i) = -\sum_{j>0} w_0(r_{ij}^0), \quad (6)$$

$i \leq 0$  is the number of an atomic layer, parallel to the surface, in the region of  $z \leq 0$ . Summation in (6) is carried out with respect to the all the lattice sites in the region of  $z > 0$ .

Excessive pressure in the subsurface region is defined as

$$P(z_i) = -\frac{1}{s_a} \left. \frac{\partial \varphi(z)}{\partial z} \right|_i, \quad (7)$$

where  $s_a$  is surface area per atom of  $i^{\text{th}}$  atomic layer.

### 3. SURFACE MELTING

To describe influence of the potential  $\varphi(z)$  on equilibrium properties of the subsurface region of the crystal, let us consider a crystal with a pairwise potential of interatomic interaction. To be specific, we consider the [100] surface of the f.c.c. crystal and an atom of the plane  $z = 0$  located in the origin. A distance between this chosen atom and any other atom located in a plane parallel to the interface  $z = 0$  is determined by the following simple equation

$$r(n, m, l) = a \sqrt{n^2 + m^2 + \left(l - \frac{\xi}{a}\right)^2}, \quad (8)$$

where  $a$  is the lattice constant,  $\xi$  is the displacement of an atom of  $l^{\text{th}}$  plane from its equilibrium position in the direction  $z$ ;  $n$ ,  $m$  and  $l$  are reduced projections of coordinates of the lattice site on the axes  $x$ ,  $y$  and  $z$ . In the case of the f.c.c. lattice,  $n$ ,  $m$  and  $l$  take on integer and half-

integer values. Approximating interatomic interaction with the Lennard-Jones potential,

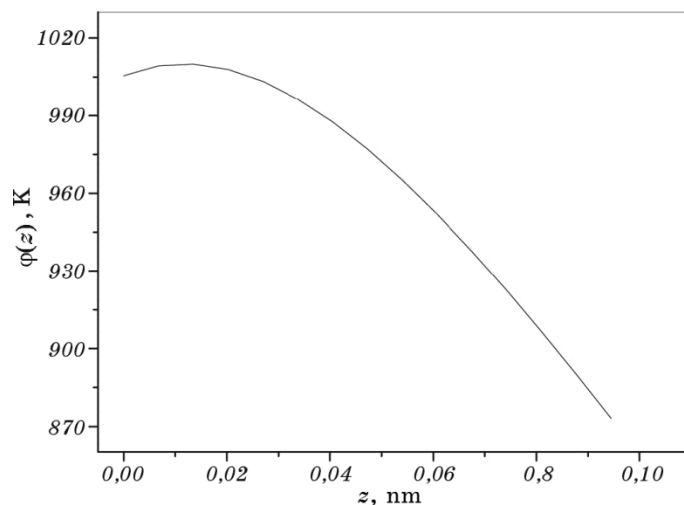
$$w(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (9)$$

we can easily calculate the dependence  $\varphi(z)$  near the surface of the semi-infinite crystal. It is important to note that this dependence is nonmonotonic (Fig. 1) due to strong influence of the repulsive part of the potential (9) at short distances from the surface.

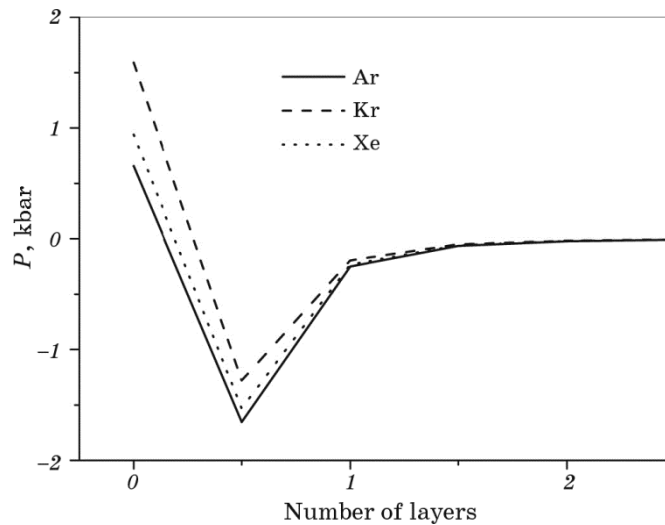
In Figure 2, we present the pressure change (7) in the subsurface region as a function of reduced distance from the surface. As follows from these results, the first subsurface layer is under rather strong negative pressure creating dilatation effect, which is partly compensated by oppositely directed bulk forces in the crystal. Therefore, negative excessive pressure acts on the subsurface region of a crystal with the Lennard-Jones potential of interatomic interaction. As follows from (2), this results in reduction of the phase transition temperature in this region.

#### 4. CONCLUSION

Though the pair potential (9) gives poor approximation of interatomic interaction in metals, the above consideration allows us to reveal thermodynamic reasons for a shift of the phase transition temperature



**Fig. 1.** Additional potential  $\varphi(z)$  within the semi-infinite Ar crystal as a function of distance from the surface.



**Fig. 2.** A change in pressure (7) acting onto crystalline planes in the subsurface region of a crystal. The parameters of the potential (9) are given in Ref. [9].

(2) in the subsurface region due to a pressure change in this region. The excessive pressure arising near the surface depends substantially on the nature of interatomic interaction in the crystal. For example, approximation of interatomic interaction in a metal with the Morse potential, which is known to describe satisfactory thermodynamic properties of Cu and Ag [10], leads to uniform compression of the subsurface region. To conclude, it is necessary to mention that introducing the additional potential  $\varphi(z)$  (6) is just a technique allowing us to calculate the excessive pressure as a function of distance from the surface.

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