

Point defects at low-index surfaces of fcc metals: Formation energies of vacancies and adatom-vacancy pairs

Yu. N. Devyatko, S. V. Rogozhkin, and A. V. Fadeev

Moscow State Engineering and Physics Institute, Kashirskoe shosse 31, Moscow 115409, Russia

(Received 27 November 2000; published 9 April 2001)

In a variety of cases the vacancy-adatom pair is shown to be the most widely spread defect on low-index surfaces due to its considerable contribution to the entropy of adatom positions. The results of calculations obtained by the modified embedded-atom and the embedded-atom methods show that the formation energy of the vacancy-adatom pair is slightly less than (or equal to) that of the vacancy for the majority of cases considered.

DOI: 10.1103/PhysRevB.63.193401

PACS number(s): 68.55.Ln, 68.35.Ja

The vacancy is usually considered as the most widespread defect on surfaces. This is a generalization of the fact that the vacancy concentration in the bulk of a metal in thermodynamical equilibrium is greater than the concentration of other defects. A vacancy in a bulk metal appears as the result of removal of an atom from its lattice position and its attachment to a step on the surface (the Schottky vacancy). In this case, the contribution of the attached atom to the positional entropy is negligible.

The situation for vacancies formed in the uppermost monolayer is absolutely different. Surface atoms have binding energy, which is essentially different from the bulk situation. This is why the arrangement of the surface atoms is different from that of the bulk atoms. There are two possibilities for attachment of the removed atom: either to a step kink or in the adatom position. If a vacancy nucleates on the surface, the adatom position contribution to the entropy cannot be neglected since it is equal to that of the surface vacancy position. This circumstance can result in another type of point defect different from that in the bulk: vacancy-adatom pairs, which have the maximum concentration in the upper monolayer. (We consider the vacancy-adatom pair where the two are separated by a large distance.) The goal of this work is to prove the vacancy-adatom pair formation is energetically preferable on some surfaces. For this purpose, let us compare the free energy of a surface with vacancies and the free energy of a surface with vacancy-adatom pairs.

In the model of noninteracting defects, the contribution of defects to the free energy consists of two parts: an additive contribution to the energy and a nonlinear contribution to the entropy (see, for example, Refs. 1 and 2). The latter is defined both by the number of possible space configurations of defects in the upper monolayer and by the variation in behavior of atoms surrounding the defect. In the case of the surface vacancy arising after attachment of a removed atom to a kink site (an analog of the bulk Schottky vacancy), the part of the free energy (F_v) of n_v vacancies created in the uppermost layer can be written as

$$F_v = n_v(\varepsilon_{\uparrow}^s - \varepsilon_k) - T \ln \frac{N!}{(N - n_v)! n_v!} - T n_v (S_{\text{ph}}^v + S_{\text{ph}}^k), \quad (1)$$

where ε_{\uparrow}^s is the energy of the detached atom and ε_k is the energy of the atom attachment to the kink site, N is the number of atoms in the topmost layer, and T is the temperature. Here and afterwards $k_B = 1$. S_{ph}^v and S_{ph}^k are the entropy changes due to the changes of behavior of atoms surrounding the vacancy and kink, respectively.

Minimization of the free energy gives the Arrhenius law for the concentration of vacancies having formation energy $\varepsilon_v^s = \varepsilon_{\uparrow}^s - \varepsilon_k$.

The part of the free energy of n_p adatom-vacancy pairs created in the uppermost layer (F_p) can be written [cf. Eq. (1)] as

$$F_p = n_p(\varepsilon_{\uparrow}^s - \varepsilon_{\text{ad}}) - 2T \ln \frac{N!}{(N - n_p)! n_p!} - T n_p (S_{\text{ph}}^v + S_{\text{ph}}^{\text{ad}}), \quad (2)$$

where ε_{ad} is the energy of atom attachment to an adatom site and $S_{\text{ph}}^{\text{ad}}$ is the entropy change due to the change of behavior of atoms surrounding the adatom. The factor 2 in the second term on the right-hand side in Eq. (2) is due to the contribution of the entropy from different possible adatom positions. In this case, the thermodynamic equilibrium concentration of pairs is

$$c_p = \frac{n_p}{N} \approx \exp\left(\frac{S_{\text{ph}}^v + S_{\text{ph}}^{\text{ad}}}{2}\right) \exp\left(\frac{\varepsilon_{\uparrow}^s - \varepsilon_{\text{ad}}}{2T}\right). \quad (3)$$

Thus, the effective formation energy of the vacancy-adatom pair ε_p^s is

$$\varepsilon_p^s = (\varepsilon_{\uparrow}^s - \varepsilon_{\text{ad}})/2. \quad (4)$$

The factor $\frac{1}{2}$ in expression (4) appears because the contribution from positions of adatoms to the entropy is equal to that from the surface vacancy positions. If the number of vacancy positions N is different from that of adatoms N' , the preexponential $\sqrt{N'/N}$ appears in Eq. (3) for the pair concentration. For the surfaces considered in our work we have $N = N'$.

If we neglect the contribution to the entropy from the change in the vibrational spectrum of atoms surrounding the

TABLE I. The formation energies of the vacancy-atom pair [ϵ_p^s (eV)] and of the vacancy [ϵ_v^s (eV)] that we and other authors obtained for various surface orientations of Ag, Cu, Ni, Pb, Al, and Pd crystals from MEAM and EAM calculations. The results of other authors are shown with references. ϵ_p^s is the vacancy-atom pair formation energy that we calculated using the results of other authors and taking into account the entropy factor. ϵ_{def} is the energy of defect formation obtained from a least-squares fit of the experimental data (Ref. 7).

Metal	Method	(110)			(100)			(111)		
		ϵ_p^s	ϵ_v^s	ϵ_{def}	ϵ_p^s	ϵ_v^s	ϵ_{def}	ϵ_p^s	ϵ_v^s	ϵ_{def}
Ag	MEAM	0.16	0.24	0.16	0.19	0.29		0.47	0.5	0.43
	EAM	0.20	0.21		0.45	0.44		0.63	0.56	
		0.21 ^{*a}	0.22 ^a		0.465 ^a	0.45 ^a		0.635 ^{*a}	0.58 ^a	
					0.43 ^{*b}	0.4 ^b	0.63 ^{*b}	0.55 ^b		
Cu	MEAM	0.25	0.28	0.35	0.33	0.42	0.35–0.5	0.64	0.64	0.7
	EAM	0.3	0.285		0.66	0.63		0.83	0.7	
		0.3 ^{*a}	0.29 ^a		0.62 ^{*a}	0.58 ^a		0.825 ^{*a}	0.72 ^a	
		0.3 ^{*c}	0.29 ^c		0.65 ^{*c}	0.59 ^c	0.84 ^{*c}	0.72 ^c		
Ni	MEAM	0.27	0.36		0.37	0.51		0.83	0.87	0.5–0.8
	EAM	0.341	0.334		0.74	0.71		0.95	0.82	
		0.34 ^{*a}	0.34 ^a		0.7 ^{*a}	0.66 ^a		0.94 ^{*a}	0.82 ^a	
		0.29 ^{*d}	0.28 ^d							
Pb	MEAM	0.135	0.145		0.18	0.24		0.345	0.33	
Al	MEAM	0.18	0.24		0.4	0.51		0.88	0.91	
	EAM	0.14 ^{*a}	0.14 ^a		0.28 ^{*a}	0.29 ^a		0.46 ^{*a}	0.39 ^a	
Pd	MEAM	0.26	0.33		0.38	0.54		0.80	0.87	
	EAM	0.275 ^{*a}	0.27 ^a		0.565 ^{*a}	0.67 ^a		0.87 ^{*a}	0.78 ^a	

^aReference 15.

^bReference 18.

^cReference 16.

^dReference 17.

defect, we easily obtain the values of the free energies (1) at (2) at their minima:

$$F_v = -n_v T, \quad F_p = -2n_p T. \quad (5)$$

Note that estimation of the entropy associated with the change in the vibrational spectrum near a vacancy and atom in copper has resulted in a value of the entropy factor of about 1 in expression (3) as obtained by Frenken, Huussen, and Van der Veen.³

From Eq. (5) it follows that, even if the concentrations of vacancies and pairs are close to each other ($c_v \approx c_p$), the global minimum of the free energy corresponds to formation of vacancy-atom pairs. To define what kind of defect is energetically favorable, it is necessary to compare the appropriate equilibrium concentrations c_v and c_p , or the energies of formation of the appropriate defects. In the case of $\epsilon_p^s \leq \epsilon_v^s$, the process of vacancy-atom pair formation is energetically preferable because $F_p < F_v$.

Calculation of the free energy (2) is similar to that for Frenkel pairs in the bulk.^{1,2} The type of defect considered (vacancy-atom) differs essentially both from the isolated (Schottky) vacancy and from the Frenkel pair. The formal difference between the vacancy-atom pair and the Frenkel pair is in the sign of the energy of the self-atom, which

plays a role similar to that of the interstitial atom in the Frenkel pair. This very difference, as one can see from Eq. (4), may lead to a situation where the formation energy of the vacancy-atom pair becomes less than the formation energy of the isolated vacancy. In this case, the process of vacancy-atom pair formation is energetically preferable, which follows from Eq. (5).

Calculations of the formation energies of isolated vacancies and of vacancy-atom pairs have been done by us for a number of metals with various surface orientations. The results (without taking into account the relaxation of surrounding atoms) are presented in Table I. Most calculations in our work were carried out using the modified embedded-atom method (MEAM).^{4,5} All parameters were taken from Ref. 4, where the fitting of the embedding function was completed. Each of the parameters used is directly related to a physical quantity: the sublimation energy, the lattice constant, the bulk modulus, two shear constants, two structural energy differences, and the vacancy formation energy in the bulk. The “bulk” functional of interaction must be used very carefully in calculations of surface characteristics. In order to test the reliability of our results we carried out some more calculations by the embedded-atom method (EAM) using a different fitting of parameters of interaction⁶ (see Table I). Note that

the MEAM gives values of the surface energy close to the experimental ones for the surfaces considered.⁴

The calculated values of the defect formation energies presented in Table I increase in the sequence (110) → (100) → (111). Within the framework of the MEAM the formation energy of the vacancy-adatom pair is slightly less than that of the isolated vacancy for the majority of cases considered. That means that the process of vacancy-adatom pair formation is energetically preferable. This is especially pronounced for the (100) and (110) surfaces. On the (111) surface this effect is small. Despite the considerable difference between the methods of fitting the parameters in the EAM and MEAM, the results do not contradict each other and the main conclusions remain the same. Within the accuracy of calculations the formation energy of a vacancy obtained from the EAM is very close to that of a vacancy-adatom pair for the (110) and (100) surfaces. However, this is also the case when the free energy of vacancy-adatom pairs (5) is twice that of vacancies, which speaks well for the pair formation.

The EAM gives vacancy formation energies for (111) surfaces and Ni(100) lower than those of pair formation. The MEAM calculations led to different results. However, if $\varepsilon_v^s < \varepsilon_p^s$, a transition from vacancy formation at low temperature to pair formation at high temperatures is possible. This transition takes place at the temperature $T_c = (\varepsilon_p^s - \varepsilon_v^s)/\ln 2$, if T_c is not higher than the melting temperature. For example, if $\varepsilon_p^s - \varepsilon_v^s \approx 0.05$ eV, $T_c \approx 700$ K. Thus, the EAM calculations support pair formation for Ni(100), Ag(111), Cu(111), and Ni(111) at high temperatures.

The formation energies of surface defects ε_{def} extracted in Ref. 7 from experimental medium-energy ion scattering (MEIS) results⁸⁻¹⁴ on the temperature dependence of the mean square displacements of atoms are also shown in Table I. The theoretical formation energy of the surface vacancy and that of the vacancy-adatom pair are both rather close to the values obtained from experiments. The energy ε_p^s is rather small on the (110) surface for Pb, Ag, and Al. Therefore, the vacancy-adatom pair concentration is already significant at moderate temperatures. So, for example, at $T = 600$ K for Ag, the concentration of pairs reaches 10%. Note that disordering of the Ag(110) surface was observed above this temperature.¹⁴ The small value of ε_p^s for Pb(110) correlates well with the low value of the surface melting temperature for this material.³

The results for the vacancy formation energy calculated by other authors using different EAM variations¹⁵⁻¹⁸ are also shown in Table I. Using these results and taking into account the entropy factor $\frac{1}{2}$ [see Eq. (4)], we obtained the values of

pair formation energy ε_p^s marked with an asterisk shown in the table. All shown values are in good accordance with our EAM calculations and support the conclusions made above. The existing *ab initio* calculations for the Al, Cu, Ag, and Rh (111) surfaces were completed only for the vacancy formation energy.^{19,20} However, within the framework of this approach, these calculations are not sufficient to make a conclusion which mechanism is responsible for the formation of defects.

The effective formation energy of a vacancy-adatom pair can be comparable to (or even less than) the formation energy of a vacancy as a result of simultaneous operation of two factors. The first is that the pair formation energy is the difference between the energy of removal of an atom from the surface and the energy of its attachment to an adatom position. The second is that the entropy of an adatom position reduces the effective formation energy by one-half. Both these factors have been discussed in literature; however, the second one has not been taken into account in analyzing the equilibrium state of the surfaces under consideration (see, for example, Ref. 17). The simultaneous action of both factors can change the equilibrium state of the surfaces. The results of calculations obtained by the MEAM and EAM show that the concentration of vacancy-adatom pairs can be higher than the vacancy concentration on the surface. As follows from expression (5), the free energy of the surface with vacancy-adatom pairs is less than the free energy of the surface with vacancies. In this case only vacancy-adatom pairs are observed on the surface. This effect is the most manifest on the (110) and (100) surfaces.

Formation of vacancy-adatom pairs on the surface can essentially change the interpretation of MEIS data. The treatment⁷ of experimental data points to an important role of point defects in the anomalies⁸⁻¹⁴ observed in the behavior of surface atoms in transition metals at elevated temperatures. The role of point defects in surface phenomena was shown in high-resolution low-energy electron diffraction studies of the Ni(110) (Ref. 21) and Pb(100) (Ref. 22) surfaces and in the scanning electron microscopy investigation of the Pt(111) surface.²³ In those experiments an anomalous decrease of the diffraction intensity accompanied by an increase of the background intensity with temperature was explained by assuming that vacancies can appear on the surface. Note that introduction of vacancy-adatom pairs in the models of Refs. 24 and 25 allowed the mean-square displacements of atoms on Ag(110) and Cu(110) surfaces to be explained. Ensemble density-functional molecular-dynamics simulations²⁶ of the Al(110) surface also speak for the generation of vacancy-adatom pairs at high temperatures.

¹N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

²R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1965).

³J. W. M. Frenken, F. Huussen, and J. F. Van der Veen, *Phys. Rev.*

Lett. **58**, 401 (1987).

⁴M. I. Baskes, *Phys. Rev. B* **46**, 2727 (1992).

⁵Y. N. Devyatko and S. V. Rogozhkin, *Vacuum* **56**, 279 (2000).

⁶S. M. Foiles, M. I. Baskes, and M. S. Daw, *Phys. Rev. B* **33**, 7983 (1986).

- ⁷Y. N. Devyatko, S. V. Rogozhkin, V. I. Troyan, E. P. Gusev, and T. Gustafsson, *Zh. Eksp. Teor. Fiz.* **89**, 1103 (1999) [*JETP* **116**, 2038 (1999)].
- ⁸R. Schneider, H. Durr, T. Fauster, and V. Dose, *Phys. Rev. B* **42**, 1638 (1990).
- ⁹P. Stairis, H. C. Lu, and T. Gustafsson, *Phys. Rev. Lett.* **72**, 3574 (1994).
- ¹⁰D. E. Fowler and J. V. Barth, *Phys. Rev. B* **52**, 2117 (1995).
- ¹¹H. C. Lu, E. P. Gusev, E. Garfunkel, and T. Gustafsson, *Surf. Sci.* **352-354**, 21 (1996).
- ¹²E. P. Gusev, H. C. Lu, E. Garfunkel, and T. Gustafsson, *Surf. Rev. Lett.* **3**, 1349 (1996).
- ¹³K. H. Chae, H. C. Lu, and T. Gustafsson, *Phys. Rev. B* **54**, 14 082 (1996).
- ¹⁴B. W. Busch and T. Gustafsson, *Surf. Sci.* **407**, 7 (1998).
- ¹⁵S. V. Eremeev, A. G. Lipnitskii, A. I. Potekaev, and E. V. Chulkov, *Phys. Low-Dimens. Struct.* **3/4**, 127 (1997).
- ¹⁶M. Karimi, T. Tomkowski, G. Vidali, and O. Biham, *Phys. Rev. B* **52**, 5364 (1995).
- ¹⁷E. T. Chen, R. N. Barnett, and U. Landman, *Phys. Rev. B* **41**, 439 (1990).
- ¹⁸R. C. Nelson, T. L. Einstein, S. V. Khare, and P. J. Rous, *Surf. Sci.* **295**, 462 (1993).
- ¹⁹H. M. Palatoglou, M. Methfessel, and M. Scheffler, *Phys. Rev. B* **45**, 1877 (1993).
- ²⁰J. Neugebauer and M. Scheffler, *Phys. Rev. B* **46**, 16 067 (1992).
- ²¹Y. Cao and E. Conrad, *Phys. Rev. Lett.* **64**, 447 (1990).
- ²²H.-N. Yang, K. Fang, G.-C. Wang, and T.-M. Lu, *Phys. Rev. B* **44**, 1306 (1991).
- ²³Y. Uchida and G. Lehmpfuhl, *Surf. Sci.* **243**, 193 (1991).
- ²⁴T. S. Rahman, Z. J. Tian, and J. E. Black, *Surf. Sci.* **374**, 9 (1997).
- ²⁵L. Yang and T. Rahman, *Phys. Rev. Lett.* **67**, 2327 (1991).
- ²⁶N. Marzari, D. Vanderbilt, A. D. Vita, and M. S. Payne, *Phys. Rev. Lett.* **82**, 3296 (1999).