

# Concept of chemical surface and vacancy-mediated exoemission

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**Abstract** This article offers a new definition of the chemical surface as a locus of vacancies and introduces the distinction between the concepts of physical and chemical surfaces. It is shown that such a formalism is more suitable for the description of some superficial properties of solid-state formations than the so-called terrace–ledge–kink model. The main part of the experimental work was measurement of thermostimulated exoemission spectra resulting from vacancy-mediated migration of superficial reagents and attempts to link the measured properties with the configurations of the chemical surface. Through analysis of the experimental results and their comparison with published data, it is shown that kinetic parameters observable by exoemission spectroscopy due to superficial migration of atomic particles are more informative than the same characteristics as determined by other modern experimental methods.

**Keywords** Vacancy · Solid surface · Chemical surface · Exoelectron emission · Thermostimulation · Kinetic analysis · Kinetics order

## Abbreviations

EE	Exoelectron emission
TSEE	Thermally stimulated exoelectron emission
TSD	Thermally stimulated desorption
STM	Scanning tunneling microscopy

## Introduction

Against the background of modern methods of surface investigation, some traditional methods have prematurely fallen by the wayside. This article deals with the physical characteristics of solid surfaces obtained by one such method, namely EE spectroscopy. The EE phenomenon is varied and has been sufficiently investigated. For a summary of relevant concepts, see the works of H. Kaambre, B. Kortov, and others collected in the proceedings of the most recent international symposium on exoemission and related relaxation phenomena [1]. We do not attempt to revise or refine known concepts but rather examine the limited use of this effect, which in our opinion, can physically reveal some fine-grained alterations of the surface configuration.

Physicists and chemists explain identical processes on a surface of condensed matter using different formalisms. According to the basic principle of translational symmetry, the concept of vacancy (later superficial vacancies) was introduced, similar to that of a broken chemical bond in the language of chemists. However, even the term “surface” itself retains some uncertainty.

The traditional concept of a vacancy will be expanded to redefine vacancies as nodes of translational symmetry that could be occupied by structural elements. Then, a new definition of a surface as a locus of vacancies can be introduced. In abstracto, the instant surface of a self-

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bonded elements system is an array of all possible one-step variations from this state. It seems appropriate to denote this the “chemical surface,” because for some objects (for example, fullerenes), the traditional physical surface and the array of superficial vacancies do not coincide. In various crystals vacancies differ from one another differently depending on symmetry types. But can be exactly classified (indexed) in terms of the number of occupied nodes in their coordination sphere. This generalization is more suitable than and has various advantages compared with the so-called terrace–ledge–kink (TLK) formalism, because the latter model only deals with a limited part of all possible elementary configurations at a local site of the surface.

### Vacancies and the chemical surface

The translational symmetry of crystals emerges as an ordering of the elements of the system. Usually, a vacancy is understood to mean a node from which an atom is removed. However, if we try to introduce the concept of a “finite ideal crystal,” it becomes necessary to redefine vacancies as nodes of the translational symmetry that could be occupied by structural elements. Using such a definition of break points of the system, in addition to the usual vacancies, we also include some nodes ostensibly located outside the crystal (only some of which were previously classified as superficial vacancies). We shall denote these as innate vacancies ( $V_i$ ), because this representation is equivalent to cutting out a finite volume from an ideal crystal.

At a certain moment in time, the system is characterized not only by its arrangement at that time but also by the states it could reach through one-step evolution. Our innovation in terms of the definition of vacancies is trivial and formal, but the role of the  $V_i$  in the surface properties of crystals is very important, as some physical properties can only be associated with such a surface configuration.

The introduced innate vacancies ( $V_i$ ) are equivalent to one or more broken (open) chemical bonds. In this regard, it is expedient to denote the proposed concept of a surface as a “chemical surface,” especially because the chemical activity of undissolved matter (solid) is determined by its surface. Such a formalism also promotes the conjugation of two different branches of science for the interpretation of some of the physicochemical properties of solid surfaces based on the concepts of chemical processes and explanations of solid-state physics based on quantum-mechanical principles.

The proposed distinction between the physical and chemical surfaces becomes important on consideration of small formations such as fullerenes. Atoms of carbon in  $C_{60}$  are spatially distributed on the surface of a sphere, but

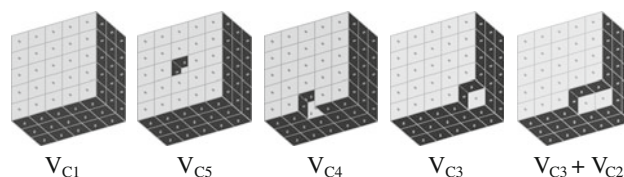
from the point of view of structural periodicity, this fullerene should be considered as only a two-dimensional self-conjugated lattice. It does not have any vacancies (open chemical bonds) and thus has no “chemical surface”. According to the terms of the proposed concept absence of vacancies is main reason for stability of such fullerenes. In usual three-dimensional periodic structures, construction of such a closed system is theoretically impossible. However, to estimate the structural stability of such forms, it would be obvious to introduce special parameters, for example, the ratio between the numerical chemical surface (the total number of vacancies) and the numerical volume (the quantity of constructing elements, atoms, or molecules).

Let us consider the classification of vacancies for a simple cubic crystal. A bulk vacancy in the volume is denoted by  $V_{C6}$ , as it is simultaneously a vacancy for six adjacent atoms. This is just only one incident when vacancy occurs alone without neighboring vacancies. In all other cases each so-called superficial vacancy belongs to the set of vacancies that form the chemical surface. Traditional bulk vacancies and/or clusters thereof could also be considered as an inner cavity.

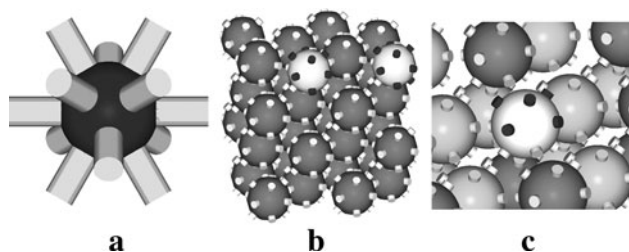
Any innate vacancy on a straight flat surface (Fig. 1) shall be denoted by  $V_{C1}$ , because it is a vacancy for only one nearest atom. A traditional superficial vacancy on a flat surface,  $V_{C5}$ , is a vacancy for five nearest atoms, whereas  $V_{C4}$  (at an edge) has four nearest atoms and  $V_{C3}$  (at a vertex) has three.

A more complicated situation occurs for face-centered cubic (FCC) lattices. In this case, the number of broken chemical bonds greatly exceeds the number of superficial atoms, because each atom is bonded to 12 neighbors in its coordination sphere (i.e., the coordination number). Chemical bonds are polarized in three different atomic planes (six in each) which in pairs form flat corners equal to  $71^\circ$  (Fig. 2a).

The superficial configuration strongly depends on the crystalline orientation of the atoms forming the local surface area. If this area corresponds to the directions of the FCC unit cell, then each atom on a flat terrace has four broken bonds and removal of one of them results in another eight. Each atom belonging to an edge and/or not extreme vertex (FCC have different vertices) has seven broken bonds, whereas atoms vertex are bonded by only three neighbors (Fig. 2b); any adatom on such a flat surface area



**Fig. 1** Simple configurations of vacancies



**Fig. 2** Configurations for FCC. Light spheres highlight differing arrangement of atoms; cylinders highlight bonds

will be bonded to four nearest superficial atoms. In this regard, the analog of  $V_{C1}$  is  $V_{FC4}$ . If the surface is formed by a  $45^\circ$  section (Fig. 2c), its atoms will have five free chemical bonds, including one oriented perpendicular to the surface. The corresponding innate vacancy can be occupied by only a singly bonded adatom, so such a vacancy shall be denoted as  $V_{FCC1}$ .

Another very important issue for consideration is the principle of the distribution of the valence electron cloud (when the number of chemical bonds is much greater than the valence number). Formally, it can be supposed that electrons jump alternately from one bond another, but how this process is regulated, especially when some of the bonds are broken, remains unclear.

The formalism introduced above can complete the TLK model by providing a more detailed representation of all possible configurations of crystalline surfaces. However, for its practical application, it is necessary to obtain corresponding experimental data confirming the occurrence of physical effects resulting from such minor distinctions.

## Experiment and analysis

To realize a situation corresponding to removal of a limited volume from a continuous substance, it is first necessary to avoid the influence of the environment; i.e., if we break a piece away from a monocrystal, it is necessary to do so in a vacuum. On the other hand, to investigate the interconversion of different types of superficial vacancies, it is better to choose an object in which such vacancies are present in abundance, i.e., a polycrystal. Finally, it is necessary to choose a method for nondestructive observation.

These requirements appear very demanding, but it seems that we can achieve some such results based on the supersensitivity of exoelectron emission phenomena. The term exoelectron emission introduced by J. Kramer reflects supposition that EE of cold-worked metals is induced by exothermic recovery processes of the objects under study [1]. Under this term, a wide range of physical processes

occurring on a surface or in superficial layers of condensed matters are combined. Directly, or by implication, vacancies practically always participate in production of exoelectrons.

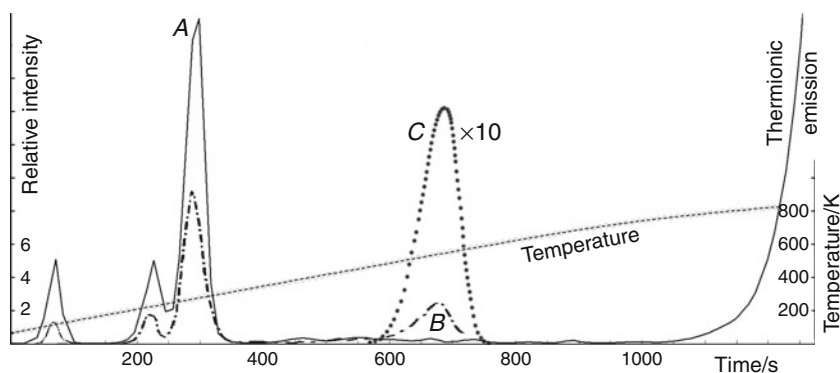
In our experiments, we observe thermally stimulated EE (TSEE) from some metals irradiated by soft X-rays. Experimental conditions and equipments are described in detail elsewhere [2]. The main goal of this experimental work is investigation of the correlation between TSEE spectra and the configuration (i.e., the distribution of particular superficial vacancies) of pure metallic surfaces. Berger [3] describes an experiment with platinum wires where exoemission was caused only by quenching of vacancies. We also try to achieve similar circumstances, but in contrast to the heavy quenching of vacancies in the bulk, we apply soft reconfiguration of the metallic surface using X-ray irradiation.

For maintenance of high thermal conductivity the substrate (oxygen less technical Copper M0 or Stainless steel) was used as the sample under investigation. In separate experiments, special metallic plates of the same material or of gold were placed over this substrate. To clean the metallic surface, we applied prolonged high-vacuum high-temperature treatment of the specimen up to its sublimation (slightly lower than the melting point of copper). After this high-vacuum thermal treatment, the substrate was cooled naturally to room temperature and then using liquid nitrogen. Soft X-ray radiation was used for EE excitation [2]. After irradiation at liquid-nitrogen temperature, the substrate was heated at constant heater power, or with a special device designed to increase the heating rate gradually. Throughout the heating process, the average values of the emission current and substrate temperature were measured and recorded after every 10 s to determine the TSEE spectrum (Fig. 3). Similarly, the pressure of residual gases was determined by measuring the thermostimulated desorption (TSD). In the temperature range 800–1,000 K, the well-known thermionic emission (TE) was also measured, which allowed calibration of the measurement chain and verification of the workfunction of the copper substrate at the initial “low-temperature” TE stage. For the described aim of the experimental work, we should first argue that the properties observed only correspond to the clean metallic surface.

Let us highlight the following experimental evidence:

1. As is well known, there was a strong difference between the TSEE results for annealed and unannealed samples. Prolonged high-temperature treatment of the specimen up to the sublimation point and its nondurable cooling under high-vacuum conditions allow one to assume that the well-reproducible low-temperature (up to 350 K) TSEE spectra is characteristic only of

**Fig. 3** TSEE glow curves of copper substrate: *A* well annealed, *B* exposed to normal atmosphere, and *C* exposed to saturated steam



- the metallic surface (measurements of the workfunction by TE also confirm the purity of the surface).
- This assumption is also confirmed by the known experimental fact that prolonged specimen storage in an atmosphere of residual gases, or under water vapor (Fig. 3), suppresses exoemission activity (in general, oxidation and/or adsorption) in the low-temperature range.
  - An equilibrium quantity of superficial vacancies cannot initiate exoemission (experiments without excitation).
  - Parallel measurements of the pressure of residual gases did not show any synchronous changes in TSEE or TSD spectra of the annealed specimen, however this does not allow one to completely exclude the possible participation of sorbents in TSEE, although TSEE is absent without preliminary X-ray irradiation, while there is no difference between the TSD results of irradiated and nonirradiated samples in this range.
  - The magnitude of the activation energy of the main emission peak as revealed by the analysis of the experimental data coincides with the known value for vacancy-mediated migration of superficial atoms in copper [4].

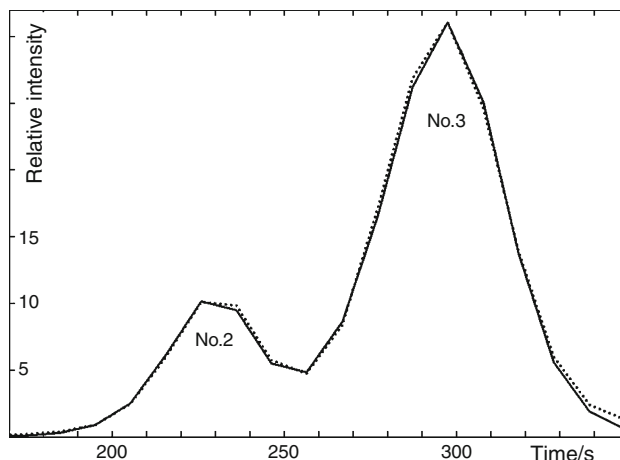
Excitation of a sample at low temperature by X-rays can cause changes of the surface configuration, i.e., redistribution of superficial vacancies. In any case, irradiation leads to energy accumulation in the lattice, and it is exactly this energy that is released during the subsequent thermostimulation, accompanied by exoemission.

To explain the exoemission mechanism, it first seems necessary to consider the criteria for resemblance to diffusion processes that occur on the surface of real samples. Among the large number of publications on this subject for comparative analysis, we chose the voluminous work by Raoul van Gastel [4] that contains a detailed description of results achieved using various physical methods, including modern scanning tunneling microscopy (STM). The kinetic characteristics are considered in the comparison.

### Kinetics

One of the main advantages of EE as a physical method is the opportunity for exact registration of the emitted electrons via direct acceleration and counting of their quantity. This enables a rather simple method for suppression of background signals and maintenance of wide dynamic range. The experimental results provide a plot of emission current versus time and/or temperature. Thereafter, by application of computer modeling based on rapid variation of some parameters (curve fitting), one can obtain acceptably accurate values of intensive (not depending on the number of elements forming the system) kinetic constants (triplets). Reference [5] provides an example where significantly differing kinetic triplets can satisfactorily reproduce the original experimental data. Except for such warning, due to its high sensitivity, EE requires observance of corresponding caution during interpretation of results and accounting for various factors in calculations [1].

Processing of the low-temperature spectrum (Fig. 4; Table 1) yields a value of the kinetic order of  $3/2$ . To verify that this process indeed obeys such a power dependence



**Fig. 4** Experimental (dotted) and calculated glow curves

**Table 1** Triplets

No.	Kinetic order	Activation energy/eV	Frequency factor/s <sup>-1</sup>
1	1.5	0.332	$3 \times 10^{12}$
2	1.5	0.717	$3.5 \times 10^{15}$
3	1.5	0.717	$9 \times 10^{12}$

(formulas are given in [2]), we tried a wide set of different functional dependences and the potential for superposition of neighboring peaks, but all the investigated alternatives exhibited consistent deviation from experimental data.

The activation energy and frequency factor values calculated by TSEE (Table 1) near room temperature practically coincide with the activation energy and attempt frequency for vacancy-mediated diffusion on copper surface as determined by Van Gastel [4] by STM measurements. However, the TSEE spectrum of Cu, as well as the mentioned emission peak near room temperature, also contains another peak (near 230 K) with the same value of activation energy but with a frequency factor almost three orders of magnitude greater. The lowest emission peak (the first one in Fig. 3) near 130 K (with frequency factor  $3 \times 10^{12} \text{ s}^{-1}$ ) has activation energy of about 0.33 eV. This value is near to the activation energy for diffusion of copper adatoms, which is about 0.36 eV according to Ref. [4].

Considering these results, the following picture seems to be the most probable: As a result of irradiation, a comparatively small number of vacancy–adatom pairs are created (the first weak TSEE peak probably being caused by adatom–vacancy recombination), whereas the main result of excitation is an unbalanced alteration of the vacancy subsystems (i.e., a redistribution of a particular number amongst the various above-mentioned vacancy types). As frequently highlighted in Ref. [4], vacancies and adatoms are formed and annihilated at steps and kinks. In terms of the proposed formalism, this corresponds to interconversion between various types of vacancies, i.e., change of the configuration but without growth of the total number. Peaks 2 and 3 in Fig. 4 are probably caused by reverse transitions of vacancies with reduction in the total free energy of the system, with the kinetics of both peaks being diffusion controlled (according to Ref. [4], in this temperature range vacancies and adatoms possess high

mobility). The different frequency factors may be caused by specific properties of the participating reagents (for example, vacancies belonging to sites with different crystalline orientation and accordingly different number of open chemical bonds).

Similar results were also obtained using a stainless-steel substrate and gold plates.

On the one hand, the choice of a polycrystalline material facilitated our task, however on the surface of such samples, zones with different crystal orientations are present simultaneously, and their contributions are mixed in the total signal. To progress with this research and to clarify the interpretation of the EE spectra, combined application of modern means will be necessary, as the unique sensitivity of EE could reinforce the results of methods such as STM. TSEE glow curves produced under thermal scanning clearly illustrate the dynamics of the observed process and provide an opportunity for the calculation of characteristic kinetic constants.

## Conclusions

The results of the presented TSEE experimental investigation on some metallic specimens and comparison with published data confirm the usefulness of the proposed formalism of a “chemical surface” for the interpretation of physical processes related to the surface configuration of crystalline materials.

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