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The effect of the tungsten surface structure on the formation of potassium clusters

© D.P. Bernatsky, V.G. Pavlov

Ioffe Institute,
St. Petersburg, Russia

E-mail: bernatskii@ms.ioffe.ru

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The influence of the surface structure on the formation of polyatomic potassium clusters on the surface of a single crystal of tungsten has been found. The cluster composition was identified using time-of-flight mass spectrometric analysis of ions formed during field desorption. The surface structure was changed by build-up the tip by heating in an electric field, in which the hemispherical tip of the tip turns into a polyhedron. It is shown that the build-up leads to a sharp decrease in the number of polyatomic clusters. Only monatomic (K^+) and diatomic (K_2^+) ions were detected, whereas on the smoothed tip the number of atoms in clusters reached eight. Most likely, the detected changes are related to the disappearance of steps on the surface. It is assumed that the formation of clusters is facilitated by an increase in the concentration of adsorbed potassium atoms at the edge of the stage due to a reflecting barrier and a potential energy well, as well as the dragging of atoms with a dipole moment into the field inhomogeneity region.

Keywords: adsorption, surface diffusion, field desorption, crystal steps, microscopy, mass spectrometry.

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1. Introduction

The study of cluster formation is related to their application in various fields of science and technology, in particular, the production of new materials, implantation, the study of nanoscale structures, crystal growth, nanotechnology, photonics [1,2]. The prospects of using ion clusters consisting of a small number of atoms as part of the primary ion beam in the method of secondary ion mass spectrometry (SIMS) are noted, which significantly increases the yield of secondary ions [3,4]. Therefore, the research of new methods for obtaining clusters is an important and urgent task. In particular, it was shown in Refs. [5,6] that low-atomic clusters of alkali metals can form on the spherical surface of refractory crystals. The studies were carried out using a field desorption microscope to obtain mass spectra of cluster ions [7]. Tungsten and rhenium tips were used as samples. From the obtained dependence of the number of observed peaks on the stress on the sample, it was found that the formation of clusters and their composition depends on the place of formation on the surface. The tips of the annealing mold used as samples have a single crystal surface similar in shape to a hemispherical surface with flat faces and transition regions with monatomic steps. From this it follows that two areas can be distinguished where clusters could originate. The formation of associations of alkali metal atoms was not observed on flat surfaces, in earlier studies of [8–10]. Therefore, it is reasonable to assume that the formation of clusters is influenced by monatomic steps located between flat faces. In order to verify this assumption, it was necessary to change the number of monatomic steps on the surface of the tip.

In this paper, the formation of potassium clusters is investigated when the shape and structure of the surface of a substrate (a single crystal of tungsten) change from a hemispherical shape with a large number of crystalline steps on the surface to the shape of a polyhedron, the surface of which consists of smooth crystalline planes.

2. Experimental procedure

To study the formation of clustered alkali metal ions on a metal surface in a strong electric field and determine their mass, a field desorption and field electron microscope were used, which provides the possibility of time-of-flight mass spectrometric analysis of ions desorbed by an electric field [7]. Figure 1 shows a scheme for registering ions formed during field desorption from the sample surface.

The formed ions (during field desorption) or electrons (during field emission) moved along radial trajectories to a detector consisting of two microchannel plates (MCP) and a luminescent screen. With the help of MCP, ion and electron currents were amplified and enlarged field desorption images or field electronic images on a nanometer scale were created on a fluorescent screen.

To measure the flight time of desorbed ions, a positive potential was applied to the tip from two sources: a constant $U_0 = 0{-}30\,\mathrm{kV}$ and a pulse amplitude $U_p = 0{-}4\,\mathrm{kV}$ and a duration of $10{-}20\,\mathrm{ns}$. The voltages are selected in such a way that there is no field desorption without a pulse at

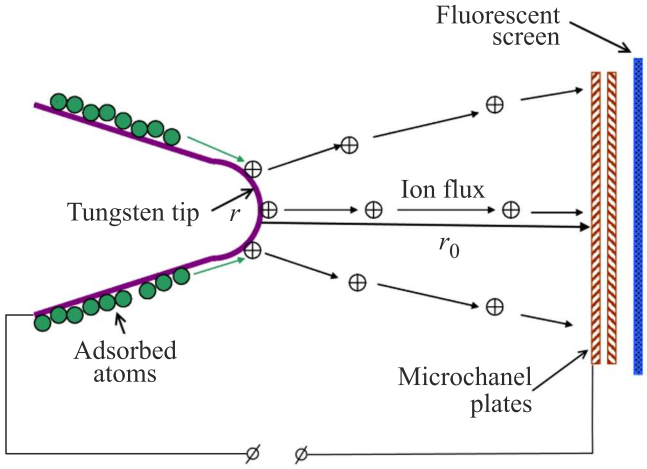

Figure 1. Scheme of field desorption and registration of ions.

constant voltage, and the addition of a voltage pulse causes desorption.

When ions hit the detector, light flashes are formed on the fluorescent screen, which are converted by a photoelectric multiplier into electrical signals. The electrical signals are sent to a storage oscilloscope, the scan of which is synchronized with a pulse voltage generator. The clock frequency of the pulse voltage was selected (taking into account the oscilloscope parameters) in the range of one hertz. Time-of-flight mass spectra were recorded by a video camera and entered into a computer.

The masses (m) of ions desorbed during the pulse were determined from measuring the time of flight (t) of ions from the sample surface to the entrance surface of the microchannel plate according to the formula $m = 2qUr_0^{-2}t^2$, where r_0 — the distance from the sample surface to the input surface of the MCP, q — ion charge, $U = U_0 + U_p$ — potential difference between the sample and the MCP, equal to the sum of the DC voltage and the amplitude of the pulse voltage.

The radius of the hemispherical surface of the tip r was ~ 500 nm, which is significantly less than the distance $(r_0 = 14\,\text{cm})$ to the MCP. This allows assuming that the desorbed ion gains all the energy $q(U_0 + U_p)$ almost at the surface of the sample.

The sample was made from a tungsten wire with 0.1 mm diameter by electrochemical etching in an alkaline solution. The wire was welded to a tungsten shackle. The resulting sample was annealed in a high vacuum (pressure $p \sim 5 \cdot 10^{-9}$ Torr) at a temperature of $T = 2500$ K. As a result of annealing, the sample was cleaned, and a tip with a monocrystalline hemispherical tip with a radius of curvature of the order of 500 nm (the tip of the annealing mold) was formed. The surface of the tip consists of crystalline planes of size 1–50 nm and transition regions between them, consisting of steps of monatomic height.

The tip was heated in an electric field to change the shape of the tip and the structure of the surface on which clusters are formed [11,12]. With this effect, the flat edges present on the surface of the initial tip expand. This process is called perestroika in Russian literature. With more intense exposure, a transition occurs from the spherical shape of the tip to a polyhedron, steps and some faces disappear, the surface consists of smooth densely packed crystalline planes (complete restructuring) [12]. In the case of tungsten, these are the planes $\{110\}$ and $\{100\}$ (Figure 2). In our case, with the orientation of the tip axis parallel to the crystallographic direction $\langle 110 \rangle$, the surface of the vertex of the rearranged tip consists of a plane (110) perpendicular to the axis and planes $\{110\}$ and $\{100\}$ at an angle 45° to the axis (Figure 2, *b*).

Figure 2, *a* shows a stereographic projection of the vertex of a smoothed tungsten tip, and Figure 2, *b* shows a diagram of the planes of the rebuilt tip. The crosses in Figure 2, *a* show the crystallographic planes located on the surface of a spherical crystal. Monatomic steps are located between the planes. When the tip is rearranged, low-index planes of the $\{110\}$ type expand, and the number of monatomic steps on the crystal surface decreases sharply. In this case, the field electronic image changes from the standard annealing shape for the tip, Figure 2, *c* to the image of the rebuilt tip, Figure 2, *d* [12].

The potential difference U required for field desorption can be estimated using the formula $U = F\beta^{-1}$, where F is the electric field strength at the tip surface, β is the electric field factor fields determined from the Fowler-Nordheim characteristics for a given tip. The electric field strength F at which field desorption occurs was calculated from the image forces model for field desorption of alkali metal atoms [13]. F can be estimated using the formula $F = e^{-3} \cdot [\Lambda(\theta) + I - \varphi(\theta) - kT\ln(\tau\nu_0)]^2$, where Λ is the heat of desorption of the atom, I is the atomic ionization potential, φ is the surface output operation, e — electron charge, θ is the degree of surface coverage with adsorbate, τ — desorption time, ν_0 is the vibration frequency, k is the Boltzmann constant, T is the temperature [6,13]. For the smoothed tip of the annealing mold in the region of submonolayer coatings with potassium, this voltage was in the range of 4–8 kV. For the rebuilt tip, this voltage will be lower due to the increased electric field strength on the sharp sections of the surface of the rebuilt tip.

The experiments were carried out at room temperature, at which the surface diffusion of potassium atoms adsorbed on tungsten ensures the restoration of the adsorbate concentration at the tip during desorption of adatoms from the surface [7]. Field desorption of adsorbate, when the voltage threshold value is set, begins from the tip of the tip in the form of an avalanche-like flash. This is due to the fact that due to field desorption, the concentration of alkali metal atoms on the surface decreases, the surface output increases, the energy barrier for field desorption decreases, and the desorption rate increases dramatically.

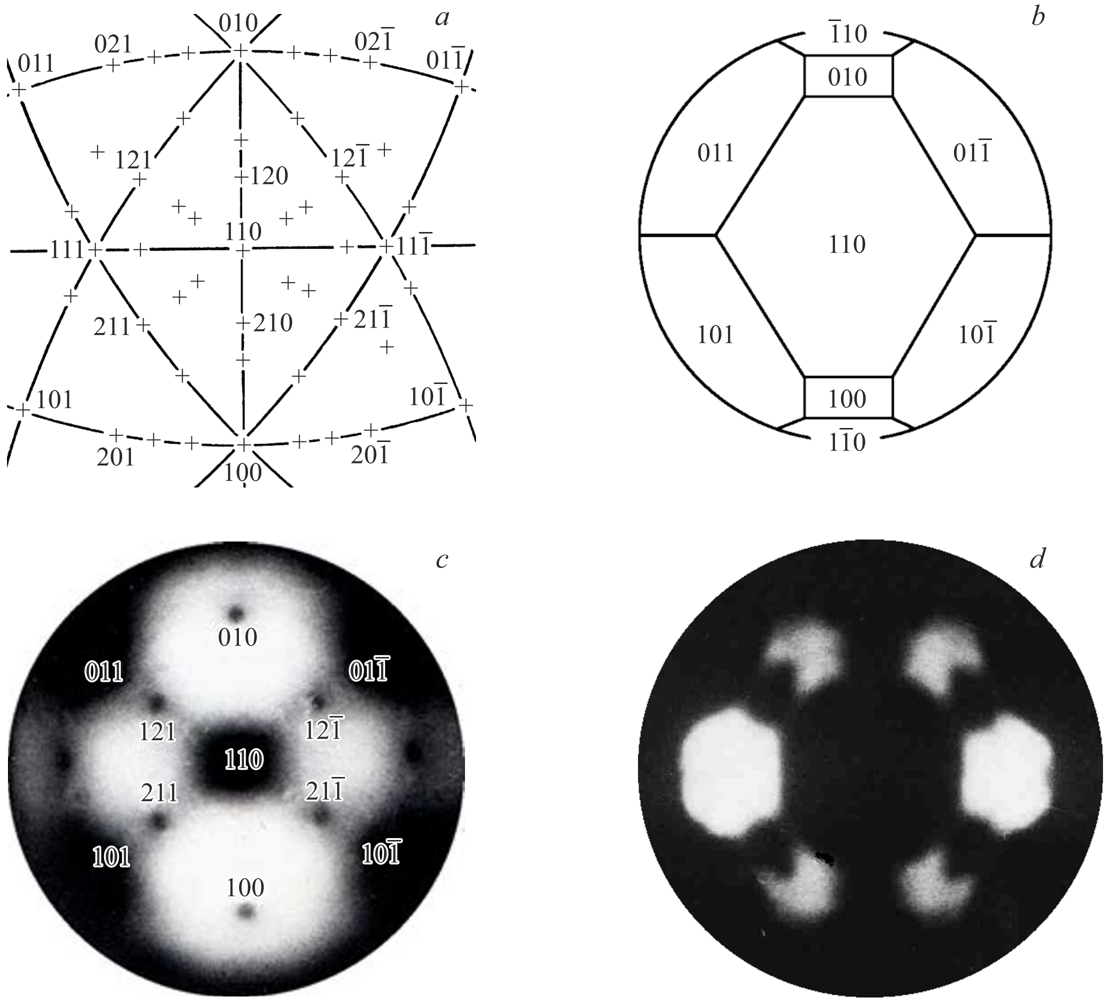

Figure 2. Vertex diagram (*a*) and field electronic image (*c*) of the tungsten tip of the annealed and rebuilt shape (*b* and *d*).

As a result, the central region of the sample is avalanche-like freed from adsorbate. However, due to the diffusion of potassium adatoms in an inhomogeneous electric field to the tip, they are desorbed at the boundary of the central region, i. e., where the electric field strength has a threshold value. Moreover, if the voltage on the sample is not changed, the field desorption process can take quite a long time due to the diffusion of adatoms from the periphery of the sample. When the voltage on the sample changes, the desorption zone can be shifted to the center (when the voltage decreases) or to the periphery (when the voltage increases). This allows scanning the desorption areas on the surface of the sample.

3. Results and discussion

The time-of-flight mass spectra obtained by field desorption of potassium from the tungsten tip of the annealing mold showed peaks corresponding to monatomic and cluster potassium ions [6]. Each spectrum could have one or more peaks. Ions containing from one to eight potassium atoms have been recorded. The mass spectra were obtained in the voltage range from 5 to 7 kV.

Field desorption of adsorbed potassium from the rearranged tip in the area of submonolayer coatings occurred, as expected, at lower voltages in the range of 2.5−5 kV. Examples of mass spectra obtained by desorption from a rearranged tip are shown in Figure 3. Monatomic and diatomic potassium ions were detected in these spectra. Clusters with a large number of atoms were not registered.

Single and diatomic potassium ions were detected at the sample voltage from the lower part of this range (2.5−3 kV). The number of diatomic ions was higher than that of monatomic ions, which may be due to the lower ionization potential of the clusters. As the voltage increased, the number of diatomic ions decreased sharply, while the number of monatomic ions increased. The processing of arrays of spectra in order to identify the effect of the magnitude of the desorbing stress on the formation of potassium ions is shown in Figure 4. The total voltage $U = U_0 + U_p$ applied to the sample is plotted along the

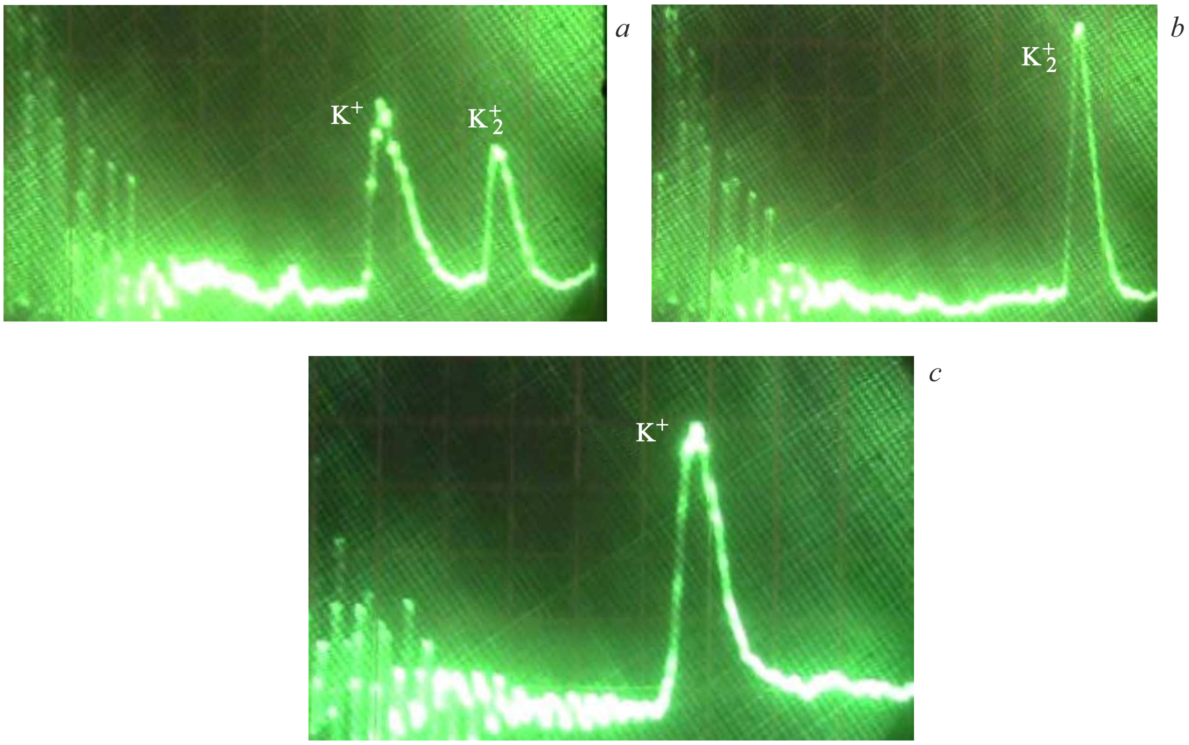

Figure 3. Mass spectra of potassium ions upon desorption from a rearranged tip at voltage: *a, b* — 3.5 kV, *c* — 4 kV.

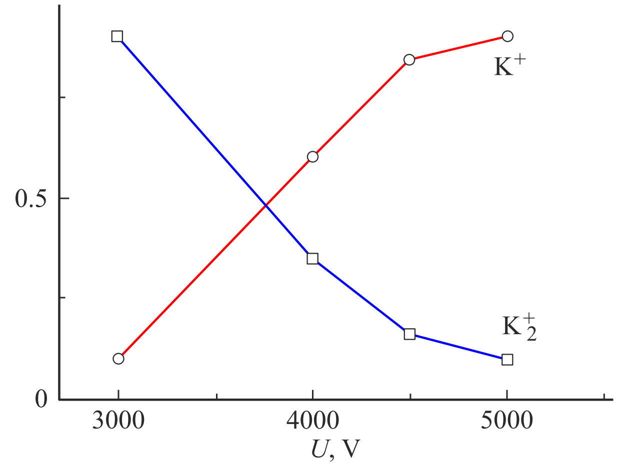

Figure 4. The dependence of the proportion of potassium ions on the applied voltage during desorption from the rebuilt tip.

abscissa axis, and the fraction of ions of a certain mass registered in the spectra during desorption at a given voltage is plotted along the ordinate axis.

At low voltages, desorption occurs from the places of the greatest field gain — corners, edges and edges of steps, i. e., where the threshold value of the electric field required for field desorption is reached. The predominant formation of diatomic clusters of potassium is observed. As the voltage increases, the desorption zone shifts to an area with a lower field gain. In our case of a rearranged tip, these are densely packed crystalline planes. Monatomic potassium ions predominate in the mass spectra under these conditions. The number of diatomic cluster potassium ions in the spectra decreases sharply. Considering that the edges of the rearranged tungsten tip [14] have narrow monoatomic steps of the plane {112}, it can be concluded that the formation of diatomic potassium clusters occurs mainly on the edges and at the edges of these steps. As the desorption voltage increases, the proportion of desorption from flat surfaces increases, which leads to an increase in the number of monatomic potassium ions in the desorption mass spectra. The absence of potassium clusters with more than two atoms on the rearranged tip may be due to the absence of wide monatomic steps, in contrast to the smoothed tip of the annealing form. The results of these experiments lead to the conclusion that steps on the surface are necessary for the formation of potassium clusters.

To explain the observed effects, we can use the results of a study of the movement of atoms on the surface of metallic crystals [15–17] and assume that an increase in the concentration (accumulation) of adsorbed atoms at the edge of the stage leads to the formation of clusters. Figure 5 shows an example of a diagram of the potential energy of an atom on the crystal surface near the edge of a step from Ref. [15]. Based on the above dependence of the potential energy of the interaction of the surface atom with the substrate, it is shown that a potential well forms in the region of the stage, and there are barriers to the

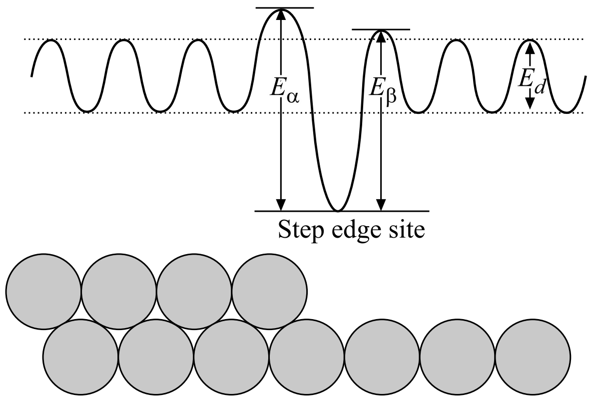

Figure 5. Diagram of the potential energy of interaction of an atom adsorbed on the surface near the stage, where E_d is the diffusion energy of the adsorbed atom, E_α and E_β are potential barriers to separation from the edge of the stage.

atom's escape from the stage. Thus, possible reasons for the accumulation of adsorbed potassium atoms at the stage include the presence of a reflecting barrier, a potential pit at the edge of the stage, and the attraction [8–11] of dipole adatoms to the field amplification site at the edge of the stage.

4. Conclusion

1. Using field desorption microscopy and mass spectrometric analysis, the effect of the surface structure on the formation of alkali metal (potassium) clusters was revealed.

2. It has been found that clusters with more than two atoms do not form on a surface consisting of smooth crystalline planes.

3. Clusters are formed when there are steps on the surface. A decrease in the area of monatomic steps on the crystal surface leads to a sharp decrease in the number of cluster ions.

4. The formation of clusters on the steps is explained by an increase in the surface concentration of diffusing adsorbed atoms at the edge of the step due to a reflecting barrier, a potential energy well, and the attraction of potassium adatoms with a dipole moment to the field gain region.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Nano Tools and Devices for Enhnsen Renewable Energy. Ed.by Sheila Devasahayam and Chaqudhery Mustansar Hussein. Elsevier, Amsterdam. (2021). 598 p.
[2] Luminescent Metal Nanoclasters. Synthesis, Characterization, and Applications. Ed.by Sabu Thomas, Kuruvilla Joseps, Saritha Appukuttan, Meegle S. Mathew. Elsevie, Amsterdam. (2022). 704 p.
[3] S.N. Morozov, U.H. Rasulev. ZhTF **83**, *6*, 45, (2013) (in Russian).
[4] S.N. Morozov, U.H. Rasulev. ZhTF **79**, *7*, 115, (2009) (in Russian).
[5] D.P. Bernatskii, V.G. Pavlov. FTT **66**, *7*, 1208 (2024) (in Russian).
[6] D.P. Bernatskii, V.G. Pavlov. FTT **67**, *8*, 1566 (2025) (in Russian).
[7] D.P. Bernatskii, V.G. Pavlov. Izvestiya RAN. Ser. fiz. **73**, *5*, 713 (2009).
[8] A.G. Naumovets. Physica A **357**, 189 (2005).
[9] L.A. Bolshov, A.P. Napartovich, A.G. Naumovets, A.G. Fedorus. UFN **122**, *1*, 31 (1977) (in Russian).
[10] O.M. Braun, V.K. Medvedev. UFN **157**, *4*, 125 (1977) (in Russian).
[11] P.C. Bettler, F.M. Charbonnier. Phys. Rev. **119**, 85 (1960).
[12] V.G. Pavlov, A.A. Rabinovich, V.N. Shred'nik. ZhTF **47**, *2*, 405 (1977).
[13] E.V. Muller, T.T. Tsong. polevaya ionnaya mikroskopiya, polevaya ionizatsiya i polevoe ispoarenie. Nauka, M. (1980). p. 218 (in Russian).
[14] V.G. Pavlov. FTT **47**, *11*, 2091 (2005) (in Russian).
[15] T.-Y. Fu, H.-T. Wu, T.T. Tsong. Phys. Rev. B **58**, *4*, 2340 (1998).
[16] G. Ehrlich, F.G. Hudda. J. Chem. Phys. **44**, 1039 (1966).
[17] T.T. Tsong, P.L. Cowan. CRC Crit. Rev. Solid State Sci. **9**, *11*, 289 (1978).

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