sensitive UV photon counters which nowadays enjoy wide use in atmospheric optics.

Beginning in 1934, low-temperature physics, and particularly the superconduction phenomenon, came to be the main concern of Shal'nikov's work. In this area, he performed several investigations which are among the most significant ones. For instance, Shal'nikov was first to discover the superconduction in very thin films of superconducting metals and a sharp rise of the critical magnetic field in these films in comparison with the critical field for bulk samples. Subsequently, these experimental findings led to the establishment of the fact, which is of fundamental significance to superconduction phenomenon, that the magnetic field penetrates rather deeply into superconductors. A I Shal'nikov completely solved the problem of the nature of the intermediate state of superconductors. In exceptionally subtle experiments, he managed to directly discover superconducting and normal domains which make up a superconductor in the intermediate state. Most recently, Shal'nikov carried out experiments which allowed him to directly measure for the first time the field penetration depth in the superconductor, which now is considered to be the most important characteristic of the superconduction phenomenon....'

The last two papers by Shal'nikov, which were published in the mid-1980s, were also concerned with the preparation technique and investigation of the properties of palladium hydride superconducting films.

Beginning in the early 1960s, Shal'nikov and his collaborator learners conducted a series of pioneering investigations in the area of quantum crystals physics. These investigations are topical in our time, too, and largely determine the face of the contemporary P L Kapitza Institute for Physical Problems, RAS.

Beginning in 1938 through 1970, Shal'nikov was a professor at Moscow State University (MSU). Under his observation, a special-purpose building equipped with facilities for the production of liquid helium and hydrogen was constructed at MSU for the Chair of Low-Temperature Physics. This allowed organization of practical training in low-temperature physics for MSU students and set up serious scientific investigations at the Chair. In May 2005, one of the lecture halls of the Physics Department building was named after Shal'nikov in memory of the educator of many generations of highly qualified physicists, who would not only generously impart his knowledge and expertise to his students, but would quite often help students and postgraduates in the solution of their everyday problems as well.

In 1956, Shal'nikov organized the publication of the new scientific journal *Pribory i Tekhnika Eksperimenta (Instruments and Experimental Techniques)* — one of the first-rate and most authoritative journals of the RAS, dedicated to the techniques of physical experiment, of which he was editor-inchief until his last days.

And, finally, it should be remembered that during the last years of his life A I Shal'nikov elaborated, in collaboration with physicians, a whole series of modern cryosurgical instruments, whose design is underlain by "brilliant experimental resourcefulness, masterly craftsmanship, and admiration for narrow gaps", which also characterized his first works.

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# Scanning tunnel microscopy and spectroscopy of an atomically clean bismuth surface

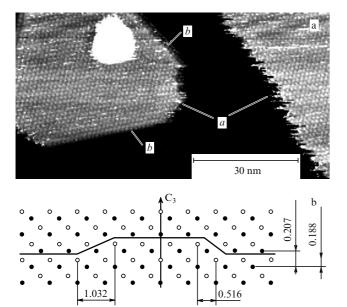
V S Edel'man

The electronic properties of bismuth have been under investigation for many decades. The spectrum of in-bulk conduction electrons has been studied in close detail (see review [1]). Considerable success has been achieved in the calculation of the band structure [2], as witnessed by the attainment of remarkable agreement with experimental data in the most sensitive region — near the Fermi surface, which requires a millielectron-volt accuracy of energy calculations. The main special feature of bismuth as a metal is that conduction electrons have a low density on the order of 10<sup>-5</sup> atom<sup>-1</sup>, their wavelength and Debye screening radius are far longer than the interatomic distance and range into the hundreds of angstroms, so that the system of conduction electrons should undergo complete rearrangement over distances of about this extent. On this basis, one would expect a radical rearrangement of the electron spectrum at the surface. Therefore, the scanning tunnel microscopy and spectroscopy (STM, STS) of the bismuth surface is of heightened interest.

The pursuance of research is facilitated by the fact that it is possible to prepare high-quality bismuth single crystals which are easily cleaved along the basal trigonal plane due to their natural brittleness. In this case, an atomically clean surface opens, where the density of foreign atoms is on the order of  $1 \ \mu m^{-2}$ . And this purity persists under high-vacuum conditions for a long time.

First and foremost, it is required to elucidate the general pattern of the surface structure formed in the crystal cleavage [3]. Bismuth is known to possess a rhombohedral structure, and its lattice may be represented as a result of the stretching of a simple cubic lattice along one body diagonal of the cube and the relative displacement of two face-centered sublattices along the same diagonal. Under this transformation, out of the four initially equivalent (111)-type planes of the cube only three remain equivalent, but they lose their trigonal symmetry and the triad axis is retained only in a single plane, the one perpendicular to the stretching direction. In what follows, these two types of planes will be referred to as quasitrigonal and trigonal, respectively.

The first results were obtained in the pursuance of investigations under room temperature conditions [4, 5]. A typical STM image of the cleavage surface is illustrated in Fig. 1. The surface is formed by atomically plane terraces, with a level difference between them being equal to or a multiple of  $0.4 \pm 0.02$  nm, because cleavage always occurs between two planes spaced further apart (see Fig. 1, at the bottom). The terrace boundaries are quite often close to the straight lines which follow the directions of atomic rows on the surface. But there also are terraces with sharply curved boundaries and nanometer-sized roundish islets (dents). One can see that at room temperature there are two systems of terrace boundaries — atomically straight (b), and made fuzzy by thermal motion (a). This difference arises from the



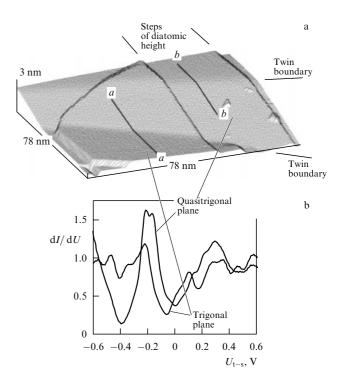
**Figure 1.** (a) Half-tone STM image of a trigonal bismuth surface, obtained at room temperature. The dark and bright regions are atomically smooth terraces located, respectively,  $\sim 0.4$  nm below and above the medium terraces. In the construction of this picture, the dark – bright gradation was selected in such a way as to reveal the atomic structure on the medium terraces. One can see that the a-type boundaries are fuzzy owing to thermal atomic motion, and the b-type boundaries remain atomically smooth at this temperature. So a different behavior arises from the fact that, as may be seen from diagram (b), the right and left boundary structures are knowingly different. (b) Atomic arrangement in the bismuth lattice in the plane perpendicular to the direction of atomic rows at the b-type boundaries.

structural difference of the boundaries (see the diagram at the bottom of Fig. 1).

To eliminate the thermal motion and stabilize the pictures under observation, as well as to avoid the thermal smearing of spectral features, the majority of measurements were performed at a temperature close to the liquid-helium temperature. The investigations were performed on a low-temperature facility [6] with the use of a scanning tunnel microscope [7].

The samples under investigation can be conventionally divided into two groups — slightly defective with a dislocation density  $n < 10^7$  cm<sup>-2</sup>, and highly defective with  $n > 10^8$  cm<sup>-2</sup>. The cleavage surface structure significantly varies from sample to sample. However, several characteristic situations can by recognized proceeding from an analysis of several dozen realizations. The patterns turn out to be qualitatively different in this case, depending on the crystal imperfection.

Two situations were observed, as a rule, in the cleavage of slightly defective crystals. Either 1-3 atomically smooth terraces with straight boundaries directed along atomic rows spread across the entire frame measuring  $1\times 1$  µm, or the terraces had the form of streaks of diatomic height (depth) and different width (sometimes only a few nanometers) stretching over the entire frame, their straight boundaries coinciding with the direction of those atomic rows whose orientation is closest to the direction of the force applied to the crystal during cleavage. Therefore, in the fast motion of a crack tip in a good crystal, the terrace boundary does not deviate from a straight line, which is



**Figure 2.** (a) STM image of a portion of a bismuth surface with a twin interlayer. (b) Differential volt—ampere characteristics of a tunnel gap for trigonal and quasitrigonal surfaces. The characteristics were measured in the translation of the STM tip along the straight lines a-a and b-b.

indicative of the conservation of its momentum in the absence of scattering.

For defective samples, the picture proves to be more diverse. First, variously shaped terraces are observed, their boundaries also coinciding with the directions of atomic rows, but the boundaries of all three equivalent orientations are equally present. Quite often there appear solitary nanoislets (and dents), like those on surfaces obtained by cleavage at room temperature. Other features may also be present within a frame, for instance, dislocations whose outcrops show up as the places of origin of new terraces [3]. And, finally, cases of twinning are also possible (Fig. 2a). Such a diversity is likely to be due to the interference of hypersonic vibrations, which are excited in the fast motion of the crack tip and scattered by dislocations. The effect is weak when the dislocations are spaced far apart, but it becomes stronger when they draw closer together and their density increases. It may be suggested that the nanoislet dimensions correspond to the characteristic lengths of the sound waves vitally important in this process.

In an STM image, a twin gives rise to a dihedral angle formed by two atomically smooth surfaces. The edge of the dihedral angle is directed approximately along atomic rows, and its experimentally found value is equal to  $(180 \pm 2.4)^\circ$  with an uncertainty of  $\pm 0.3^\circ$  caused primarily by the inaccuracy of STM piezoscanner calibration. This picture is in complete agreement with the well-known bismuth twinning scheme [8].

There are two ways to determine which of the planes observed in the twinning correspond to the trigonal plane, and which to the quasitrigonal planes. When the quality of both the surface and the STM tip permits us to observe the atomic structure, a perfect triangular lattice corresponds to

the trigonal plane. For quasitrigonal planes, there are bound to be observable isosceles triangles with the same base but with an apex angle of  $57.24^{\circ}$ , elongated perpendicular to the interface. This difference is numerically small, the heights of the triangles should differ by only  $\sim 5.8\%$ . This is precisely the picture observed in experiment [3]. The other possibility consists in analyzing the ratio between the step heights which should be equal to 0.395 and 0.374 nm, respectively, on the trigonal and quasitrigonal planes, according to crystallographic data. This small difference is quite reliably registered in experiment [9].

As would be expected, the difference in atomic structures of these two planes should result in different electronic properties. This is clearly manifested in the volt-ampere characteristics (VACs) of the tunnel gap. Depicted in Fig. 2b are differential VACs which reflect, as is well known, the density of electronic states. These characteristics were recorded at many points in the movement of the STM tip along the lines a-a and b-b. They coincided with each other to within the noise in the measurements within the boundaries of the flat portions of the corresponding crystallographic planes.

It is significant that for both planes the density of states at the Fermi level, i.e., for a voltage of 0 V, is of the same order of magnitude as for the other voltages. Thus, there forms a two-dimensional metal at the surface, and its characteristics are knowingly not as anomalous as the bulk bismuth characteristics. The transition from the spectrum typical of the trigonal plane to the spectrum typical of the quasitrigonal plane takes place in 2-5-nm wide domains at the twinning boundaries. Proceeding from this dimension, by taking advantage of the uncertainty relation it is possible to estimate the momentum of conduction electrons: it cannot be smaller than  $\sim 1-2$  nm<sup>-1</sup>. This value exceeds the momentum of bulk conduction electrons by an order of magnitude or more. Similar qualitative conclusion was borne out in photoelectron spectroscopy experiments [10].

Although in the differential VACs at the twin boundaries it is possible to distinguish separate maxima and minima which are missing from the characteristics away from the boundaries, they are not defined clearly enough to state with assurance that a one-dimensional electronic structure is formed here. The boundary of terraces is another matter (Fig. 3). The distinctions are so strong in this case that the conclusion about the formation of one-dimensional metallic structures is unquestionable.

In this experiment, the STM tip was moved in steps along a line approximately perpendicular to the terrace boundary, and the Z coordinate was measured at each point, then the feedback controlling the tip position along the Z was turned off and measurements of the VAC were made for a fixed tip – sample spacing. In this way, there resulted a family of characteristics related to coordinates on the surface and to its relief. The effect of proximity to the boundary on the electronic properties may be clearly seen by plotting VAC array sections for several selected voltages (Fig. 3a). One can see that a change in the electronic spectrum in narrow domains at the boundaries approximately 1 nm in width occurs. Consequently, the domain with a different spectrum has in fact a width of about 1-2 interatomic distances, i.e., is really one-dimensional. The structural difference of the left and right boundaries as discussed in the foregoing manifests itself also in the electronic characteristics. It is pertinent to

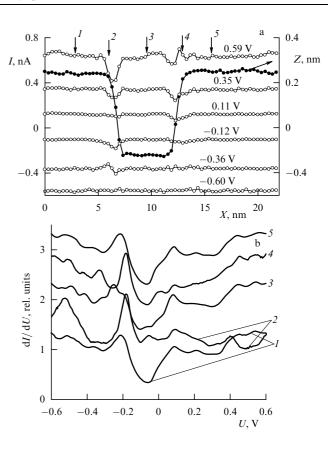
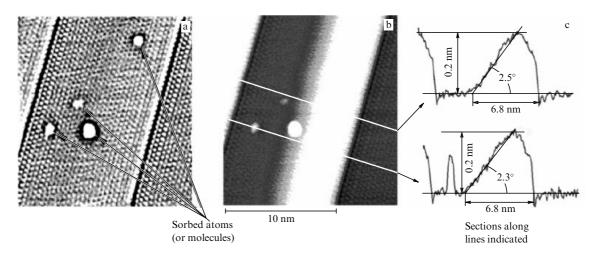


Figure 3. (a) Sections of a family of volt—ampere characteristics at several selected voltages measured in the movement of the STM tip along the line intersecting a 'groove' of diatomic depth, whose relief Z(X) is shown in the same plot. (b) Differential volt—ampere characteristics at the points indicated by arrows in Fig. 3a, the numbers alongside these arrows corresponding to the numbers of the characteristics.

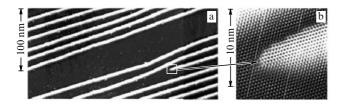
note that the initial conditions in the measurement of characteristics (voltage and current) were set at -0.6 V. The VAC section corresponding to this voltage is therefore indicative of the noise level and the reproducibility of measurements.

Changes in the spectrum are clearly visible in differential VACs. In particular, the peak for -0.22 V typical of dependences I and 5, which were obtained for flat regions, shifts to a voltage of -0.18 V, undergoes a sharp narrowing, and rises in amplitude. The behavior near 0 V qualitatively changes: a minimum in curve 2 and a peak in curve 4 are observed instead of a monotonic growth of dI/dU in other curves (Fig. 3b). In this case, in all instances the density of states at the Fermi level remains finite, i.e., electrons are delocalized along the boundary direction. It is worth noting that the spectrum in the narrow dent (curve 3) is also somewhat different from the spectrum on the 'shores'. It seems likely that this is a manifestation of the proximity of terrace boundaries, which 'lock' electrons, and this proximity is responsible for the interference of their wave functions.

Interpretation of the above-outlined results calls for a serious theoretical analysis, because it is necessary to consider the current spreading, through a one-dimensional structure, over a surface and in a volume, from a point into which the electrons tunnel. The very registering of 'one-dimensional' peculiarities forces to arrive at a qualitative conclusion about a very high electrical conduction along the boundary region with a low sectional area.



**Figure 4.** (a) Differentiated image of the twin microinterlayer in Fig. 4b. Differentiation enables a clear revelation of the atomic structure. One can see that the boundary goes precisely along an atomic row. (b) Half-tone image of a twin microinterlayer (the light streak across the center of the drawing). At the upper left corner is a portion of one more microinterlayer. (c) Sections of the relief along the lines whose position is indicated in Fig. 4b.

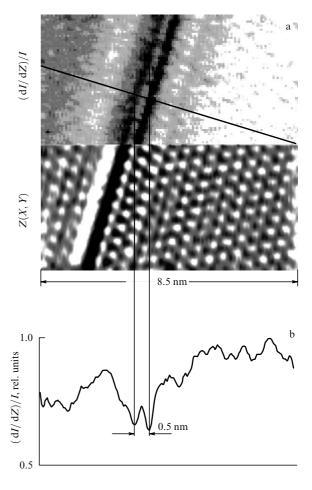


**Figure 5.** (a) Image of several microinterlayers (the light streaks). (b) Highly magnified region near the end of the interlayer. The upper sharper edge corresponds to the 'steep' boundary (see Fig. 4). The straight lines in Fig. 4b are drawn through atoms residing in the trigonal sections. One can see that the atoms at the steep interlayer edge are displaced by about 1/3 of the lattice spacing due to the longer atomic structure period, perpendicular to the boundary for a quasitrigonal interlayer surface.

The most interesting and unexpected phenomenon discovered in the experiments is the occurrence of twin microinterlayers of quantized width (Fig. 4). Their width is determined by the fact that atomic layers in the interlayer, which are inclined by a small (2.3°) angle to the layers in the remaining crystal that are oriented perpendicular to the trigonal axis, are 'matched' at the boundaries. And only the uppermost layer, which is 'matched onto' the matrix on one side, forms a 0.2-nm high step on the other side [11, 12].

Attempts to directly measure other geometrical interlayer characteristics did not meet with success. The interlayer lengths along the surface may be coarsely estimated by dividing the doubled length of all interlayers within the frame by the number of their end points. For the situation depicted in Fig. 5, we obtain a characteristic length of order 5  $\mu$ m. For the picture given in Refs [11, 12], in which many end points are discernible, the estimation yields 1  $\mu$ m. The structure of an interlayer near its end is shown at the right of Fig. 5. It is seen to gradually come to naught on both sides, the fractures at the boundary following in several interatomic distances. It would appear natural that the interlayer goes down to a depth not less than the length within which it terminates on the surface, i.e., through a distance of about 10 nm.

According to the data of Refs [11, 12], in a region with a width of one to two atomic rows near a step, like in the case of



**Figure 6.** (a) The lower part of surface image frame is 'matched' to the upper part of the frame of the tunnel current derivative with respect to the tip—sample Z-distance. (Both full frames, each occupying the whole image plane, were taken in the course of the same experiment.) (b) Section along the line shown in the image (a).

terrace boundaries, the volt-ampere characteristics are significantly different from those observed away from the singularity: for a sample-STM tip voltage lower than approximately 0.3 V they become practically linear, which

testifies to the formation of a one-dimensional conductor with a substantially higher conduction electron concentration than on the remaining surface.

An experiment aimed at measuring the quantity  $(\mathrm{d}I/\mathrm{d}Z)/I$  gives the idea of how narrow the region of an electronic spectrum singularity near the boundary is. This measurement is realized by applying to the STM piezoelectric cell, which displaces the tip in the Z direction, an alternating voltage with a frequency that lies above the feedback band, and by measuring the variable signal amplitude as a function of the surface X, Y-coordinates. In the quasiclassical tunneling model, the current is an exponential function of Z, with the exponent proportional to  $W^{1/2}$  (W is the work function). Consequently, in the above experiment, the work function versus surface coordinates is measured.

As is evident from Fig. 6, variations in the exponent are rather high. In this case, immediately at the boundary there is an anomaly only about 0.25 nm in half-width, which is even somewhat less than the interatomic distance. Therefore, at the boundary there forms a minimal-width conductor — one atom in width.

The experiments outlined above furnished extensive data on the structure of peculiarities on the surface of a cleaved facet, which reflects on the atomic scale the processes occurring in the rupture of a metal, and on their specific electronic properties.

#### Acknowledgments

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Special thanks are due to A I Shal'nikov. Not only did he bring up my teacher M S Khaikin, but over many years he also took part in my formation as a scientist and person by his advice, criticism, interest, and support of work, in the initial stage, on scanning tunnel microscopy in the Institute for Physical Problems of the USSR Academy of Sciences. And it has been a pleasure and an honor to present this report at the session of the RAS Physical Sciences Division dedicated to his centenary.

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# Impurity nanocluster structures in liquid helium

L P Mezhov-Deglin

### 1. Introduction

The first experiments aimed at the preparation and study of the properties of impurity nanocluster condensates in superfluid helium-II were pioneered by A I Shal'nikov and staged in Chernogolovka in the early 1970s [1-3]. Shal'nikov's original idea of attempting to prepare a film of atomic (metallic) hydrogen by the condensation of H atoms on a substrate cooled to a temperature T on the order of 1 K looked quite attractive. It was well known, for instance, that thin bismuth films deposited in a vacuum on a substrate cooled to  $T \approx 4.2$  K are superconductors, although bismuth under ordinary conditions makes up a semimetal with a low density of free charge carriers. However, these films are metastable and recrystallize on substrate heating above 20 K. so that on being subsequently cooled the film resembling a massive sample behaves like a semimetal. Is it possible to prepare a quasi-two-dimensional film of atomic hydrogen by depositing H atoms on a solid substrate cooled below 1 K? How is it possible to localize free hydrogen atoms on the substrate surface and minimize the probability of their subbarrier tunneling accompanied by  $H + H \rightarrow H_2$  recombination of atoms that find themselves at the neighboring sites? Will such a film of atomic hydrogen possess metallic conduction and all the more superconduction? The answers to such questions could be provided only by a direct experiment which would be hard to stage even nowadays. As we are aware today [4], recombination of atomic hydrogen restricts the maximum content of free H atoms in threedimensional deuterium-hydrogen condensate samples impregnated with superfluid HeII, which are prepared by condensing a gas beam that contains hydrogen and deuterium atoms on a superfluid liquid surface. The content is limited by the values of  $n_{\rm H} \sim 7 \times 10^{17} \, {\rm cm}^{-3}$ , so that the relative content of H atoms in the molecular  $H_2/HD/D_2$  matrix, which forms the gel frame (solid skeleton of the gel), does not exceed 1%.

Shal'nikov discussed the possibility of arranging the research work in this area, which lies at the interface between low-temperature chemistry and physics, with staff members of several Moscow institutes, in his native Leningrad Fiztekh, and lastly in the Institute of Solid State Physics (ISSP) in Chernogolovka, to whose high-capacity low-temperature base formation he had largely contributed. It was agreed that the low-temperature facility would be assembled at the ISSP, while the high-temperature atomic hydrogen source ('dissociator') for it would be possible to make at Fiztekh. However, the initial work plan had to be radically changed with time. We are reminded that in the early 1960s, during the formation period of the scientific center of the USSR Academy of Sciences in Chernogolovka, research into the methods of accumulation and storage of free radicals, including the atoms of molecular gases in molecular matrices in the simplest case, were on the list of the main research areas of the future center. Interest in this research was stimulated by the fact that its findings in case of success might be used, for instance, to increase the specific momentum of the fuel for