THE INFLUENCE OF MICROGRAVITY ON THE GROWTH OF GASB CRYSTALS

Dr. Soulayman Soulayman[+]
Dr. Leda. L. Regel[♦]

ABSTRACT

Bridgman method was applied, for growing a GaSb crystal under Micro-gravity condition (MG), on the cosmic orbital station "Mir" during the cosmic Syrian-Soviet flight. The mentioned experiment was called "Aphamia" and was carried out using furnace "Crystal". The same experiment was simultaneously carried out at laboratory condition in order to compare obtained crystals and to determine the influence of MG on the growth of GaSb crystal. During this experiment the growth of GaSb crystal with a given conductivity under Earth and MG conditions was performed. The crystal structure, impurity distribution and electro-physical properties of GaSb, were investigated. A comparison with available data in literature is also provided.

[+] **Professor At Professor At Higher Institute Of Applied Sciences And Technology, Damascus-Syria**
[♦] **Professor At Department Of Electrical And Computer Engineering, Clarkson University, USA**

تأثير الجاذبية الميكروية على نمو البلورات GaSb

الدكتور سليمان سليمان♣
الدكتورة ليدا ريغل♦

ملخص

طبقت طريقة بريدجمان لتنمية بلورة GaSb تحت شرط الجاذبية الميكروية (MG) على المحطة المدارية الفضائية "مير" أثناء الرحلة الفضائية السورية – السوفيتية المشتركة. سميت التجربة المذكورة "أفاميا" ونفذت باستخدام الفرن "البلوري". أنجزت نفس التجربة في نفس الوقت في الشروط المخبرية بهدف مقارنة البلورات التي تم الحصول عليها وتم تحديد تأثير الجاذبية الميكروية على نمو البلورة GaSb. أثناء هذه التجربة، تم تنمية البلورة GaSb بناقلية معينة تحت الأرض وبشروط الجاذبية الميكروية. تم اختبار البنية البلورية وتوزع الاشابة والخواص الفيزيائية–الالكترونية للبلورة GaSb. قورنت النتائج التي حصلنا عليها مع المعطيات المتوفرة في المراجع أيضاً.

1. Introduction

♣ أستاذ في المعهد العالي للعلوم التطبيقية والتكنولوجيا، دمشق– سورية.
♦ أستاذ في قسم الهندسة الكهربائية والكمبيوتر– جامعة كلاركسون–أمريكا.

During the second half of 20-th century there has been a considerable interest to grow semi-conducting materials under microgravity (MG) in order to obtain better-quality crystals with fewer defects and with more homogeneous distribution of impurities. This was done to obtain better electro-physical properties of the crystals. There is a practical interest in obtaining such unique high quality crystals, i.e. in the development of improved quality semi-conducting materials. This interest turned into the main argument in favour of the expensive space experiments. The initial experimental results under MG influenced significantly the development of fundamental research of crystal growth under suppressed gravitational convection.

The experiments were carried out on about 20 various semiconductors [1,2]: a) Atomic Ge and its alloys (GeTe, GeSe), b) Compounds of the type $A^{II}B^{V}$ and $A^{III}B^{V}$ (ZnSb, GaSb, GaAs, GaP and solid solutions on their base), c) $A^{II}B^{VI}$ (CdTe, CdSe), d) $A^{IV}B^{VI}$ (PbTi, SnTe), e) Solid solutions Te-Se, Bi-Sb and ternary compounds (Bi2(TeSe)3, BiSbTe, PbSeTe, CdHgTe, CdHgSe, GaZnP). Some of these substances were widely used by scientists for their experiments, for example, Ge with impurities and compounds of the type $A^{III}B^{V}$ are the most widely used, whereas some substances were used only once in experiments. The choice of materials was often prompted by the experience of using a definite substance on the Earth and by the initial good-quality material being available. The desire, to grow more perfect crystals than those, grown on the earth, and to study the effect of gravitational convection on crystal growth on the Earth with the aim to change the crystal growth technique, was also an important factor influencing the choice of materials.

However, the crystallization processes under MG and the real structure of crystals, grown under MG, have some peculiarities, caused by heat- and mass-transfer. Here, one can mention the following [3]:

a) Growth of $A^{II}B^{VI}$ compounds from gas under MG makes stoichiometry somewhat different from that of crystals, grown on the Earth, apparently, due to the greater effect of diffusion.

b) Growth from solutions under MG is characterized by the capture of greater amount of gas inclusions than on the Earth. The same is true for melts. Mutual attraction and intergrowth of crystals have morphological indications. A possible reason for this lies in the fact that pulse transfer, during crystallization, is proportional to the growth rate which is lower for those parts of the surfaces of two growing crystals that face one another and have a very narrow gap in-between.

c) Melt does not wet walls of ampoules under MG (Ge, Zn, Sb in quartz ampoules). The question thus arises about the reason of this phenomenon. Here, it was suggested that it is due to the greasing (with carbon, for instance) and roughness of walls in ampoules.

d) Distribution of impurities in the process of growth from melt is characterized by smaller amplitude zoning which, however, does not disappear totally. General distribution of impurities along the axis of a cylindrical crystal, grown by directed crystallization, is purely diffusive or "Pfann-like". These phenomena can result from MG instabilities and also from Marangoni convection.

e) Dislocation density in crystals, grown from melt under MG, is by 2-4 orders of magnitude lower than that under Earth conditions. It is thought that this phenomenon is due to non-wett $A^{III}B^{V}$ wet-ability of ampoule walls with melt. This, however, appears insufficient since growth dislocations are mainly caused by inner thermal tensions in crystals.

As it was mentioned semiconductors of the type $A^{III}B^{V}$ are the most widely used, because of their importance in opto-electronic techniques. On the base of these compound semiconductors lasers, infrared radiation sensors and solar cells are produced. In this work, we deal with GaSb which has direct energy gap of 0.74 eV. GaSb and its solid solutions were the subject of a lot of investigations which are mainly orientated for using then in transmitting and receiving units of fiber-optic communication lines as well as in photo-diodes and other applications [4]. Each application requires semi-conducting material with a number of required properties, like an appropriate forbidden energy gap, concentration distribution of impurity elements, charge carrier's concentration and mobility.

The first experiment with growing GaSb under MG conditions was the Hungarian-Soviet experiment called "Etvish" [5-7]. This experiment was carried out using Bridgman method of crystal growth taken place, with furnace "Crystal" on the Soviet orbital station “Salute-6". The temperature gradient at the crystallization front was $60^{o}C/cm$ and the growth rate was 0.188 mm/min. The Earth analog of the cosmic one consisted of long crystals, with the growth orientation defined by the axe of the ampoule. The cosmic one was a bi-crystal of a very good quality. The authors of the mentioned experiment confirmed that, in addition to the structure amelioration, the cosmic sample had improved electro-physical parameters. However, mono-crystal was not obtained during "Etvish" experiment, perhaps, because of missing a mono-crystal seed. Moreover, the behaviour of doping impurity was not investigated.

The second MG GaSb experiment was the German experiment "ES-323" [8, 9]. This experiment was done with the mirror-beam furnace (MHF) and carried out using floating zone method of crystal growth. According to the authors of this experiment, floating zone method has some advantages in comparison to the Bridgman method:

- Lower vapor pressure over the melt.
- Lower amount of stoichiometric defects, because of decreasing crystallization temperature.
- Lower dislocation density.

Authors mentioned that the impurity distribution (in this experiment $n=10^{18}$ cm^{-3}) in the Earth sample was of a banding form. The parameters of growth were:

- Growth temperature 530^{o} C.
- Growth rate 4.5 mm/day.
- Crystal diameter 10 mm.
- Length of floating zone 6 mm.

However, the length of crystal, grown under MG, was only 150–200 μm because of apparatus break-down.

Authors of the ES-323 experiment [8, 9] gave the following conclusions:

- The non homogeneous distribution of impurities in cosmic sample is less intensive than in the Earth analogue.
- Banding distribution of impurity is practically not observed in the cosmic sample because of sample rotation during the experiment.

As we see these two experiments did not give a definitive answer about the possibility of obtaining a high quality crystal structure and a homogeneous distribution of impurity when growing GaSb crystal under MG condition, even though some positive elements could be seen. Therefore, we took into consideration two positive factors of the mentioned experiments, namely: orientated crystallization using Bridgman method and seed using. The mentioned experiment was called "Aphamia" and was carried out using furnace "Crystal" on the orbital station "Mir" during the Syrian-Soviet cosmic flight. The goals of this experiment were:

- The growth of GaSb crystal with a given conductivity under MG condition.
- The investigation of crystal structure of GaSb, grown under MG condition and the impurity distribution in this crystal.
- The investigation of the electro-physical properties of GaSb, grown under MG condition.

To compare the morphology, structure, and physical properties of semi-conducting crystals grown under MG and on the Earth scientists used up-to-date well tested physico-chemical methods: electronic microscopy and electronic spectroscopy, radio spectroscopy, X-ray diffraction methods, methods for dislocation revealing by selective etching and electro-physical investigations of semiconductors within a wide range of temperatures. We use similar techniques to study our samples. The investigations were performed in years 1985-1989.

2. Equipment and materials for experiment

The technique of crystal growth in space requires specific equipment and instruments, whose power consumption, sizes and weight should be minimal. Moreover, heating and cooling modes should be automatically controlled to be easily operated by cosmonaut-operators. Besides, the safety engineering requirements should be taken into account, because, for instance, a possible explosion of ampoules with melts can destroy the space-ship and be of danger to cosmonauts.

The limitation of power consumption caused several restrictions on the ultimate temperatures of heaters operated in space. The accuracy of temperature control in such furnaces appears to be lower than that in the Earth furnaces. The designs of the available and developed installations are diversified. They are gradient and isothermic, mirror-beam and universal multipurpose furnace. Anyway, the installation used in the experiments under MG has reduced capabilities than those on the Earth. In our experiment we used the universal multipurpose furnace, called "Crystal", which fulfilled the requirements of GaSb orientated crystallization from melt. The melting temperature of GaSb is 706^{o}C.

When selecting the temperature profile of growing process we faced two opposite factors. First, for decreasing the quantity of structural defects in a grown crystal we have to lower the temperature gradient in melt near the growth zone. Second, for ascertain the doping we should limit the possibility of temperature fluctuations at the inter-phase boundary (liquid-solid), which means the increase of temperature gradient near the growth zone, or the increase of seed dimensions. At the same time we had to decide about the method of temperature control during the crystallization. We had two possible choices: programmable cooling of heating units or sample programmable pulling along the axe of the furnace. The first choice was preferred, as the movement of the container with material increases the levels of micro-accelerations.

The measured temperature gradient in a furnace "Crystal" is shown in Fig.1 while the temperature profile is demonstrated in Fig.2. It is seen, from Fig.2, that the maximal temperature (850 ^{o}C) could be obtained within one hour. Then it was constant for two hours. Zone of required gradient is obtained using two heating units of temperature (500 ^{o}C). At the crystallization front (with temperature 710 ^{o}C) the temperature gradient is 20 ^{o}C/cm in the zone of melt and 40 ^{o}C/cm in the zone of seed.

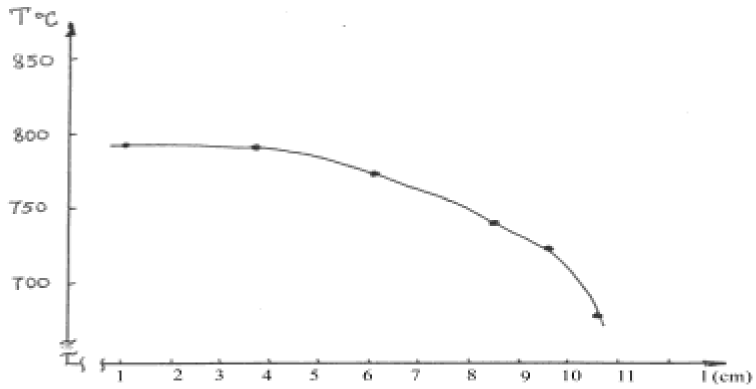

Figure 1. The measured temperature profile along the axis of the furnace.

It should be mentioned here that the diameter of GaSb crystal was chosen to be of 7 mm. The length of the seed was 10 mm. Seed of a cylinder shape was taken from a GaSb crystal, grown using the method of Czochralski in the direction (111). In order to clean its surface from oxides $1HNO_3$:2HF:$1CH_3COOH$ was used. The GaSb material was synthesized at the Soviet Institute of Cosmic Research in Moscow. The p-type GaSb was synthesized from Ga and Sb while that of n-type was synthesized from Ga and Sb and 1% of Te. The synthesis was done in quartz ampoule of 7 mm in diameter. The vacuum in the ampoule was 0.01 Torr. The control of synthesized materials was provided using XRD and metallo-graphic methods. The construction of ampoule used in experiment Aphamia is shown in Fig.3, while the construction of that used in synthesis is shown in Fig.4.

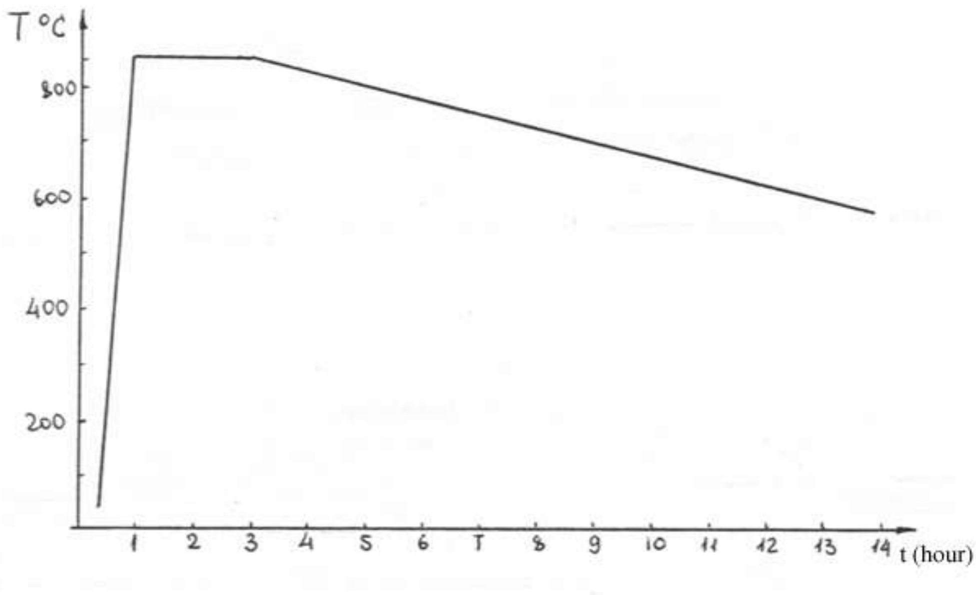

Figure 2. The temperature profile during the experiment.

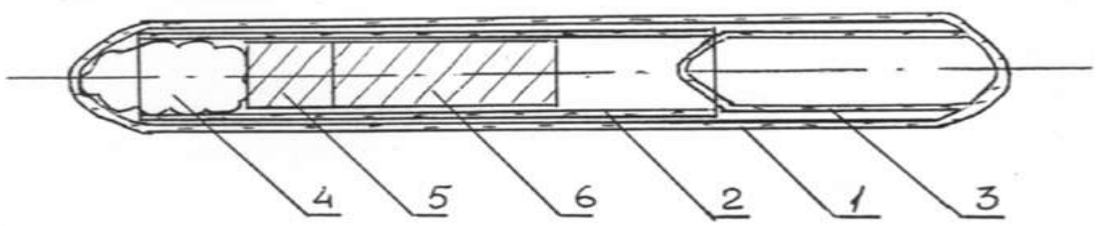

Figure 3. The construction of ampoule used in experiment Aphamia. 1 is quartz ampoule; 2 is quartz block fitting; 3 is quartz stop; 4 is kaolin wool; 5 is seed and 6 is charge.

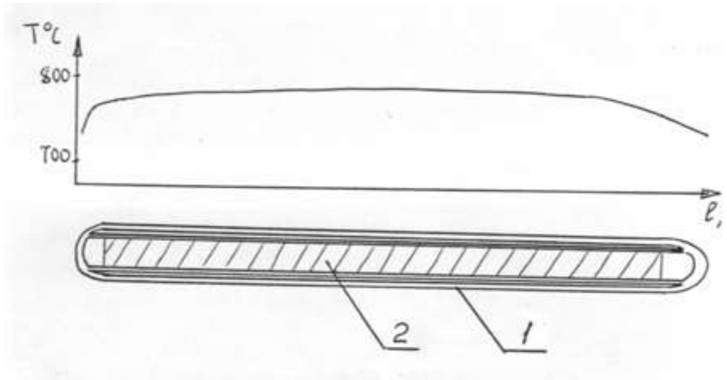

Figure 4: The construction of ampoule used in synthesis. 1 is quartz ampoule and 2 is Ga+Sb.

3. Experimental results

During the experiments the axis of the furnace was chosen to be vertical in order to eliminate the possibility of seed disconnection from charge. So, the growth axis of GaSb was orientated in opposite of the force of gravity.

3. 1 Surface structure and surface morphology

After experiment, samples in quartz ampoules were photographed (see Figs. 5-6). We did not observe any kinds of distortion. The experiment was successfully carried out on the Earth surface. At cosmic station we could do only one experiment: the growth of GaSb of n-type from a seed of p-type, because of a local failure. After that, GaSb crystals were taken off from the ampoules and also photographed directly and after rotation by 45^o (see Figs. 7-10). It is seen from these Figures that the surface structure of the cosmic sample is quite different from the surface structure of the Earth analogue. This is firstly related to the initial growth zone. We observed in the samples, grown under MG condition (see Fig.9) two recesses, symmetrically located from the axis, which surface has a coarse structure with a lot of ridges. The major part of these ridges is orientated along the axis of the crystal. The boundary of the recesses has not a right form. When studying these recesses with microscope, it was found that the boundary of the recesses is sharp. This can be due to melt super-cooling at the beginning of crystallization. As the volume of liquid GaSb is smaller than that of the solid phase and melt tries to take a more suitable form from thermodynamic point of view. This form is a sphere due to the beginning of the crystallization the growth rate is, probably, much higher than the experiment. Another factor could also take place. Under MG condition the form of liquid state of materials is very sensitive to the different types of mechanical loads which could lead to the micro-accelerations at the port of cosmic station. One can add also different types of temperature fluctuations inside and outside of the melt.

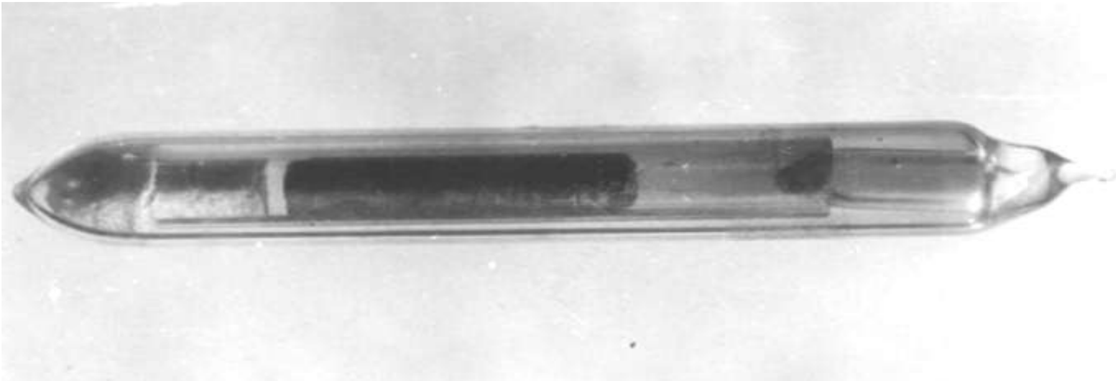

Figure 5. Quartz ampoule with GaSb Earth analogue.

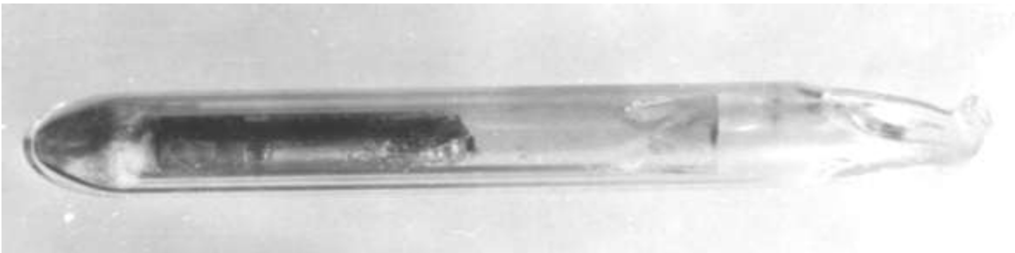

Figure 6. Quartz ampoule with GaSb Earth analogue.

Figure 7. Surface structure of Earth sample

Figure 8. Surface structure of Earth sample

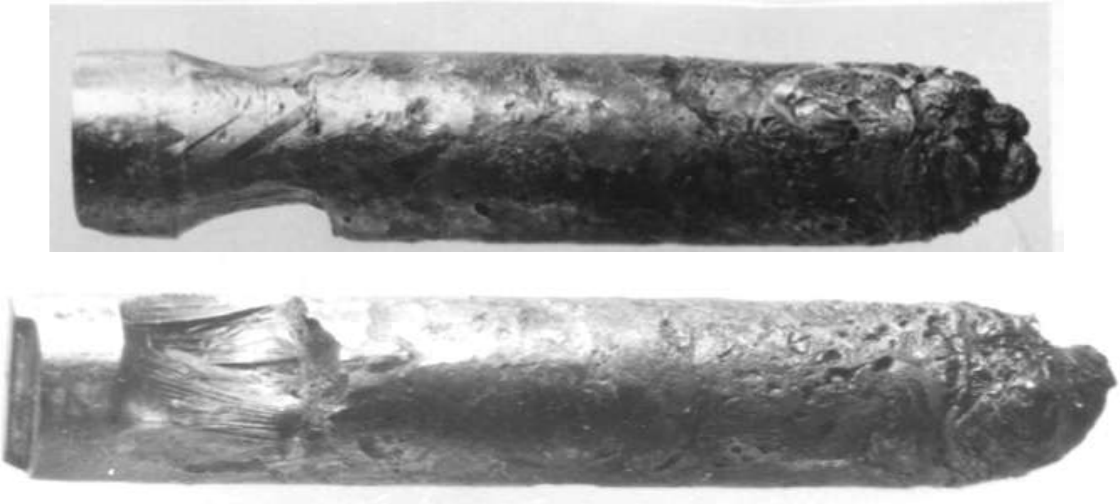

Figure 9. Surface structure of cosmic sample

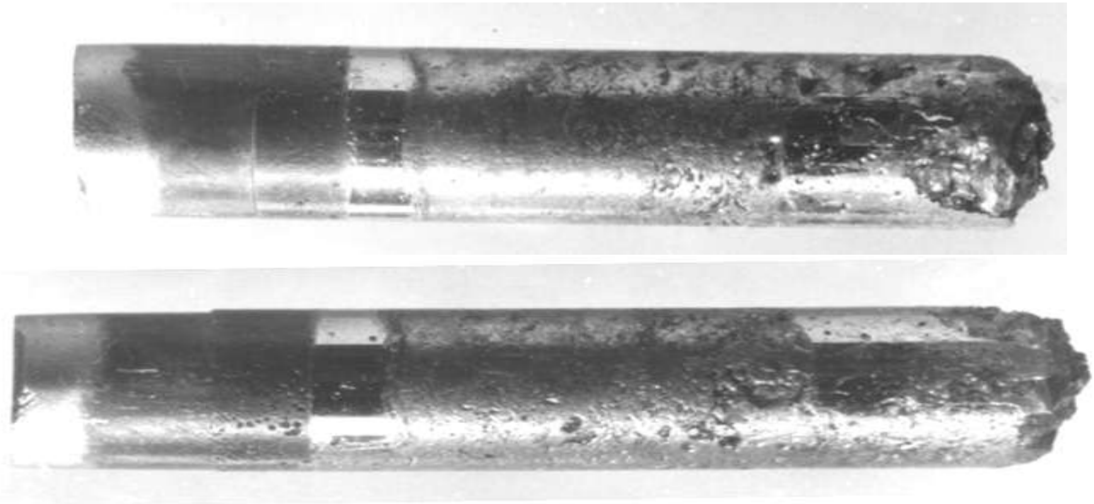

Figure 10. Surface structure of Earth sample, grown with n-type seed.

The above mentioned factors lead us to the following conclusion. Because of the high rate of crystal growth at the beginning of crystallization we obtain a block structure instead of mono-crystal GaSb during the cosmic experiment. This idea has been affirmed when studying the surface structure of the cosmic samples in details. The block structure is clearly shown on Figs 11-14. Moreover, we can mention that these blocks have a laminar structure, with layers being parallel to each other. This can be clearly seen in the zone of nicks, while these blocks could not be seen at the surface of the sample at its middle region (see Fig. 14), and their form becomes orientated.

Concerning the Earth analogue, we did not observe any of the above mentioned peculiarities. The surface structure of the Earth samples is smooth (see Figs 15-17) without any macroscopic recesses or ridges. On the other hand, one can clearly observe the boundary of the seed and that some fibers lay-out random on the surface. This phenomenon can be explained as follows. During the process of sample heating in ampoules, partial surface oxidation occurred because of residual oxygen in the ampoules. At melting temperature of GaSb oxide film does not melt, but will be broken and moved towards the ampoule walls. After crystallization the sample takes the ampoule form, with the broken parts of the oxide film (see Fig. 16).

Crystal, grown using seed of n-type and charge of p-type, has a small ring at the initial interface between seed and charge. It is wider in this case (see Fig. 17). Moreover, we observed at the surface of this crystal a lot of very small recesses, distributed statistically along the length of a melting zone. The dimensions of these recesses are less than 1 mm. This kind of recesses is also observed on the surface of the cosmic sample, but they are mainly distributed at the end of the sample. For comparison between cosmic sample and its Earth analogue one can take a look on Figs 18 -19.

Figure 11. Surface structure of cosmic sample with 4^x magnification.

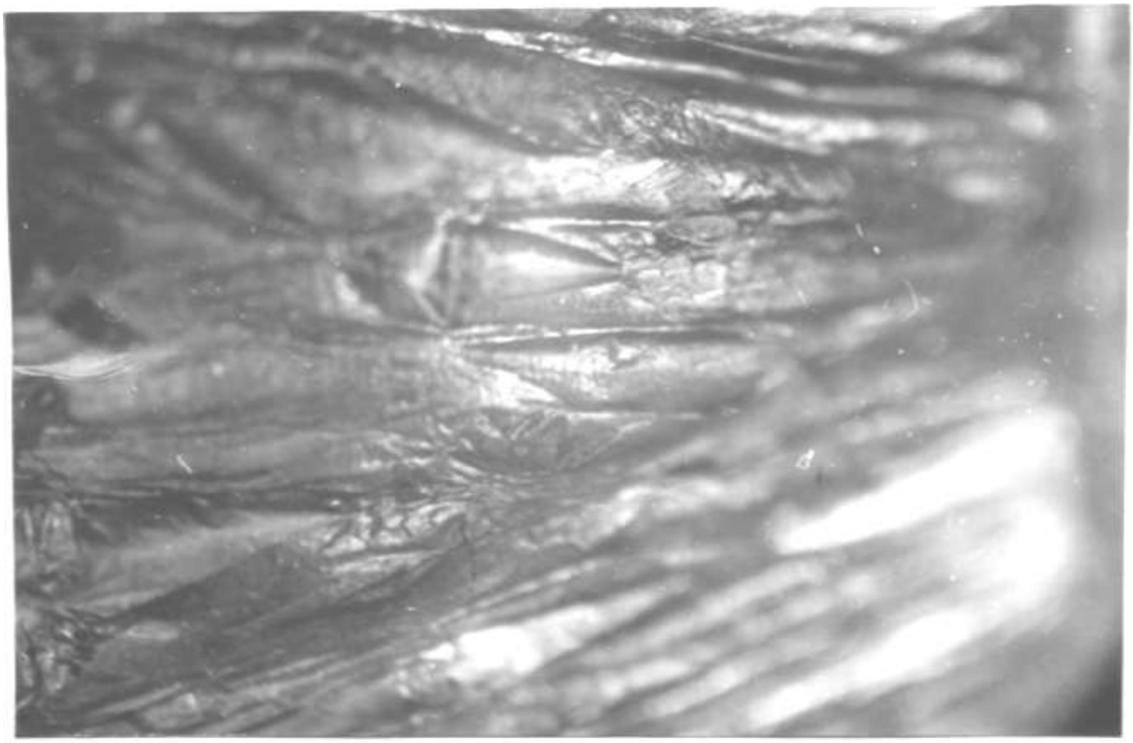

Figure 12. Surface structure of cosmic sample with 4^x magnification.

Figure 13. Surface structure of cosmic sample with 4^x magnification.

Figure 14. Surface structure of cosmic sample with 4^x magnification.

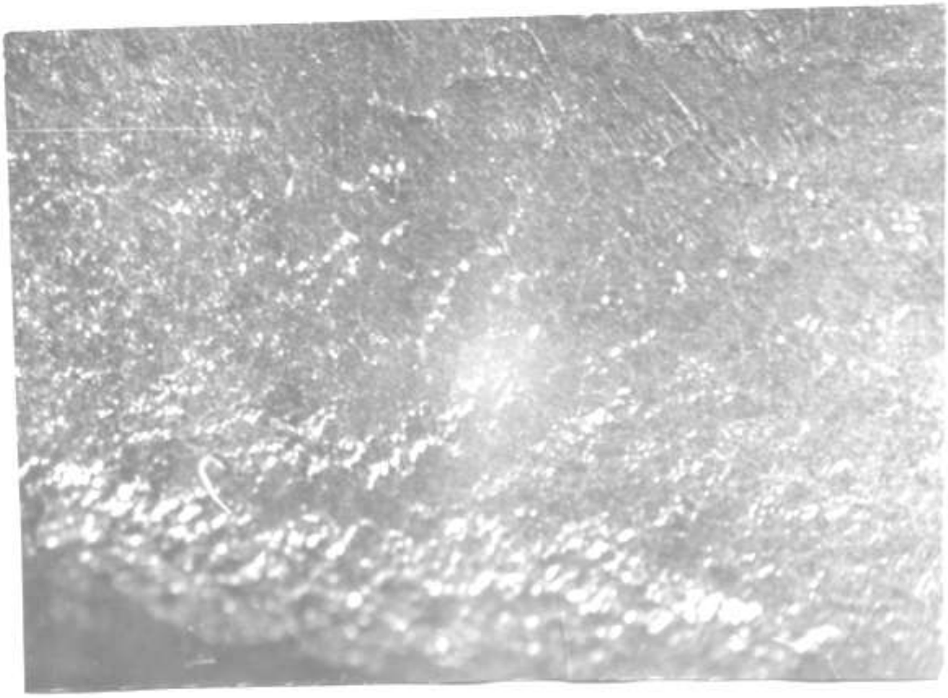

Figure 15. Surface structure of the Earth analogue of GaSb crystal with 4^x magnification.

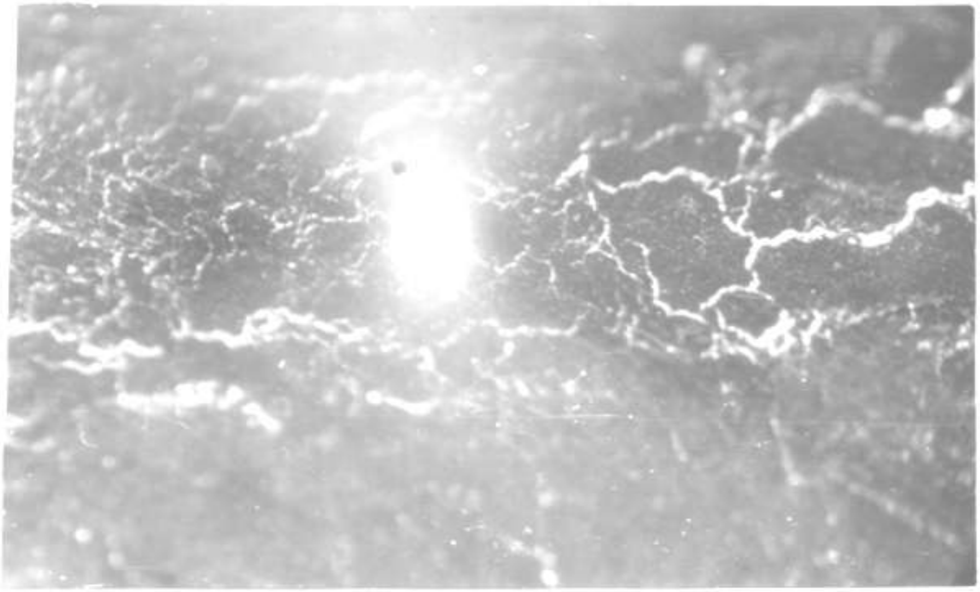

Figure 16. Surface structure of the Earth analogue of GaSb crystal with 4^x magnification.

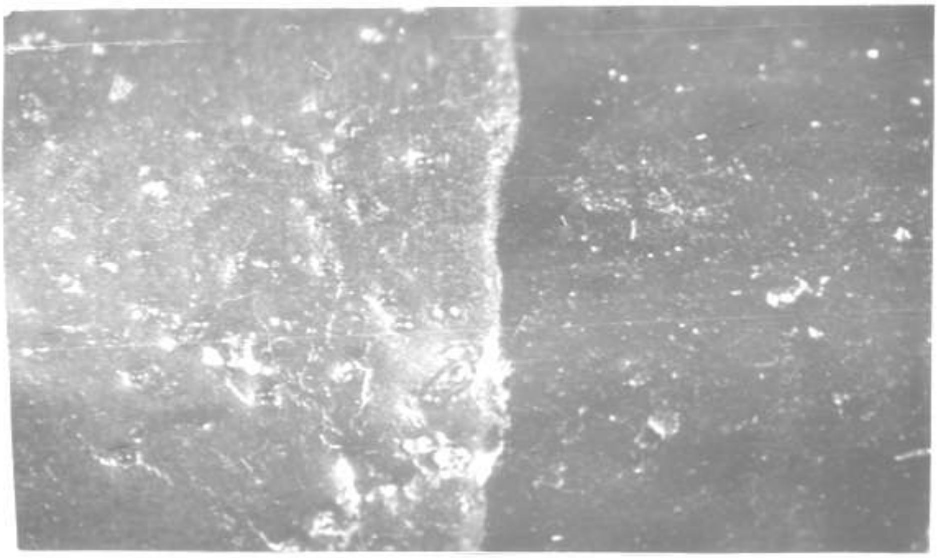

Figure 17. Surface structure of the Earth sample, grown with seed of n-type (4^x magnification).

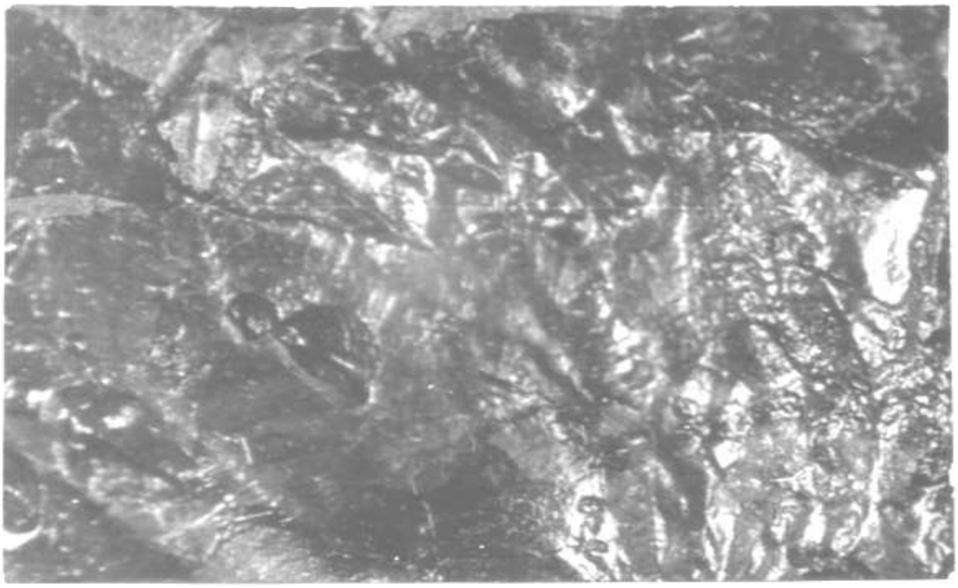

Figure 18. Surface structure of cosmic sample with 4^x magnification.

Figure 19. Surface structure of the Earth analogue with 4^x magnification.

The studies of the structure of cosmic sample and its Earth analogue using optical microscope, with 100^x magnification, did not give an useful information, as the surface structure shows a homogeneous relief. In order to determine the fine surface structure of the mentioned samples their surfaces have been treated by an etching material CP-4. The surface of the cosmic sample became less bright while the surface of the Earth analogue became brighter. This fact indicates the larger concentration of defects at the surface of the cosmic sample.

3.2 Electro-physical properties

Electro-physical investigations of the cosmic sample and its Earth analogue were performed in two steps.

First, we determined the type of conductivity of the obtained samples. In this aspect we used double-contact thermal sonde and microvolt-ammeter of compensated type as a registration unit. In the case of cosmic sample we obtain the p-type conductivity in the zone of non-melted seed while the n-type conductivity is observed along the other part of the sample. In the case of Earth analogue we have obtained the same results. When the growth is done using a seed of n-type and a charge of p-type, the type of conductivity did not change except the seed melted zone.

Second, in order to analyze the impurity distribution in the samples, their resistivity has been measured along the samples. The results are shown in Fig. 20. Fig.20 shows that there is no practical difference in the values of electrical resistivity between cosmic sample and its Earth analogue. The main difference between two samples is the uniformity of resistivity. The electrical resistivity of the cosmic sample is more uniform. For the Earth analogue the increased non-uniformity of electrical resistivity is observed in the GaSb crystal grown with n-type seed. This finding could be explained as the result of non-uniform distribution of Te concentration all over the sample.

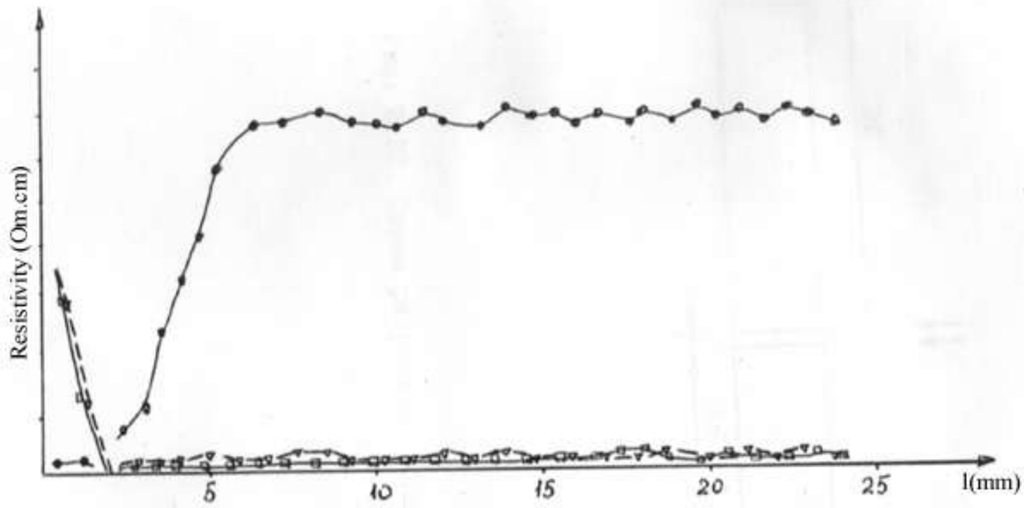

Figure 20. Samples resistivity (Ohm.cm). ● for sample, grown with seed of n-type; □ for cosmic sample and ∇ for Earth analogue.

3.3 Structure investigation

In order to study the internal structure of the obtained crystals, a cross section specimen was done at 20 mm from the beginning of the seed, as shown in Fig. 21. After that the disk surfaces have been smoothed and polished. Then they were etched using CP-4 at room temperature. The photos of the structure are given in Fig. 22-24. As it is seen, from these figures, the structure has a block form in the two samples. The average dimensions of the blocks are a few mm in the cross section.

The structure of all samples is characterized by strips, observed in different zones of the surface of cross section specimen, and finished at the surface. Moreover, some blocks are orientated to the axis of crystal. This fact indicates that the crystallization process is started from the center to the surface.

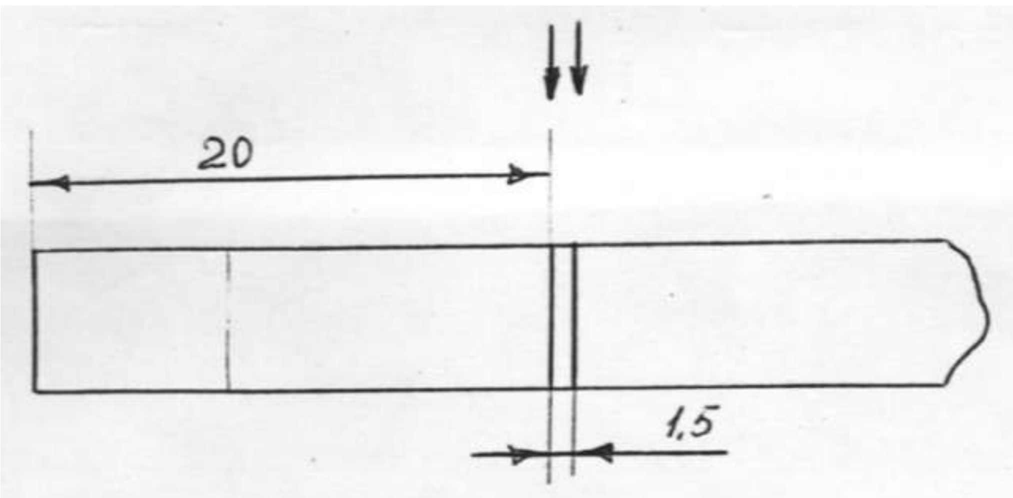

Figure 21. The scheme of the sample cut.

The main difference between sample, grown under MG condition and that grown on the Earth surface is the absence of a clear boundary between regions of different types of defects. These regions could not be different blocks as this case leads to a very thin straight line. In our case we did not observe straight lines or lines in general (see Fig. 24). Another kind of difference is observed. This is the laminar structure of the crystal, grown under MG. In Fig. 25, this phenomenon is observed as parallel dark bands. These bands are practically absent in the Earth analogue. So, metallo-graphic investigation of the samples indicates the absence of mono-crystalline structure in all samples.

Conclusions:

On the basis of our results we conclude the following:

1- Micro-gravity has an influence on the surface structure and surface morphology of the crystal, grown under MG condition.

2- Micro-gravity does not have any practical influence on electrical properties of crystals. This will be treated in detail in the near future.

3- Micro-gravity has an influence on the uniformity of the values of electrical resistivity along the sample. The values are samples grown under MG condition are more uniform than those of the Earth analogue.

4- Micro-gravity has an influence on the inner structure of the crystal.

5- Crystals grown under MG condition are more perfect than their Earth analogue.

6- Space material science experiments are still attractive and they can lead to the required results when eliminating problems explored by different experiments. This is why we can conclude that the work done by Chinese scientists [10] is quite important.

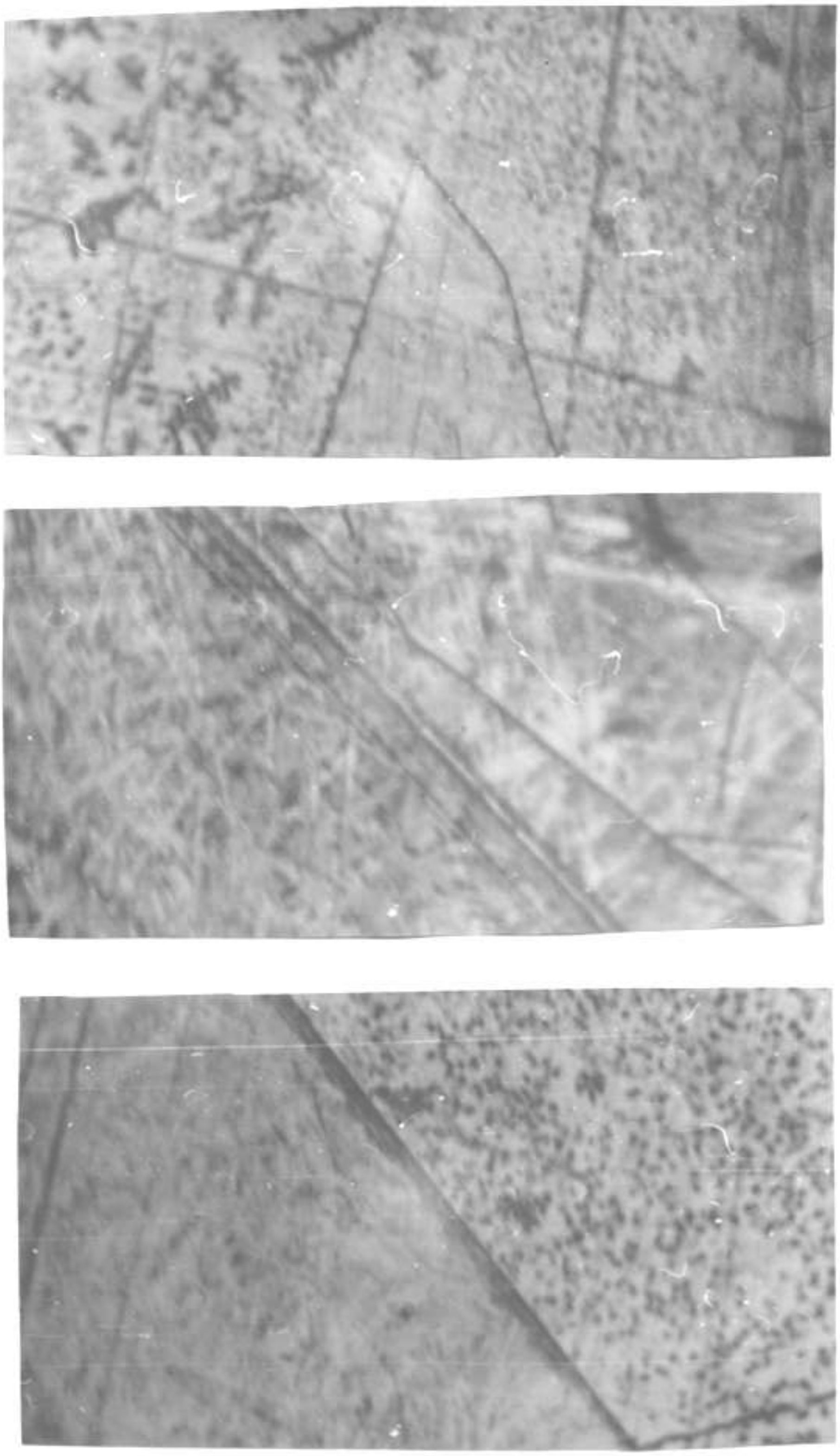

Figure 22. The structure of cosmic sample GaSb (with 100^{x} magnification).

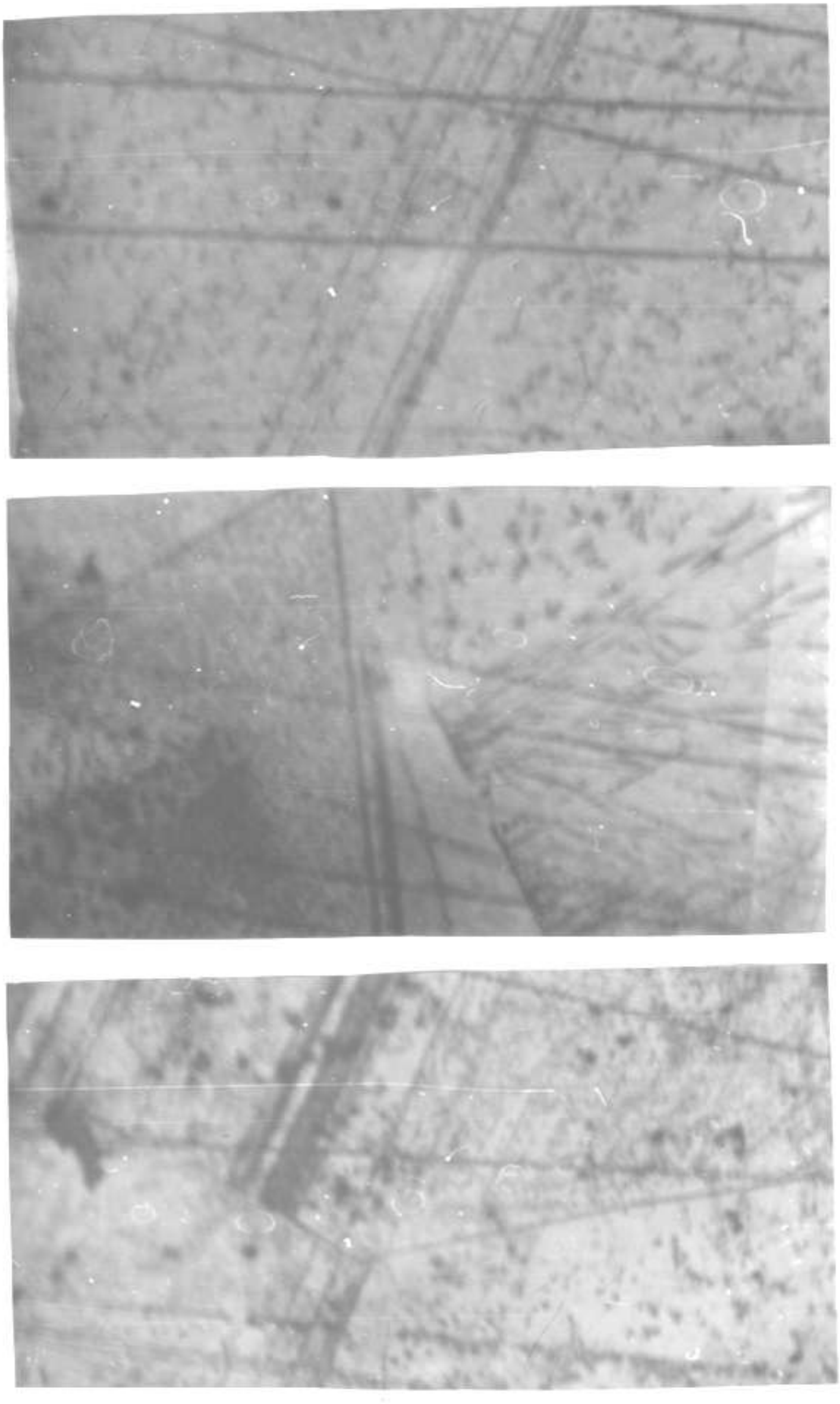

Figure 23. The structure of Earth analogue GaSb (with 100^x magnification).

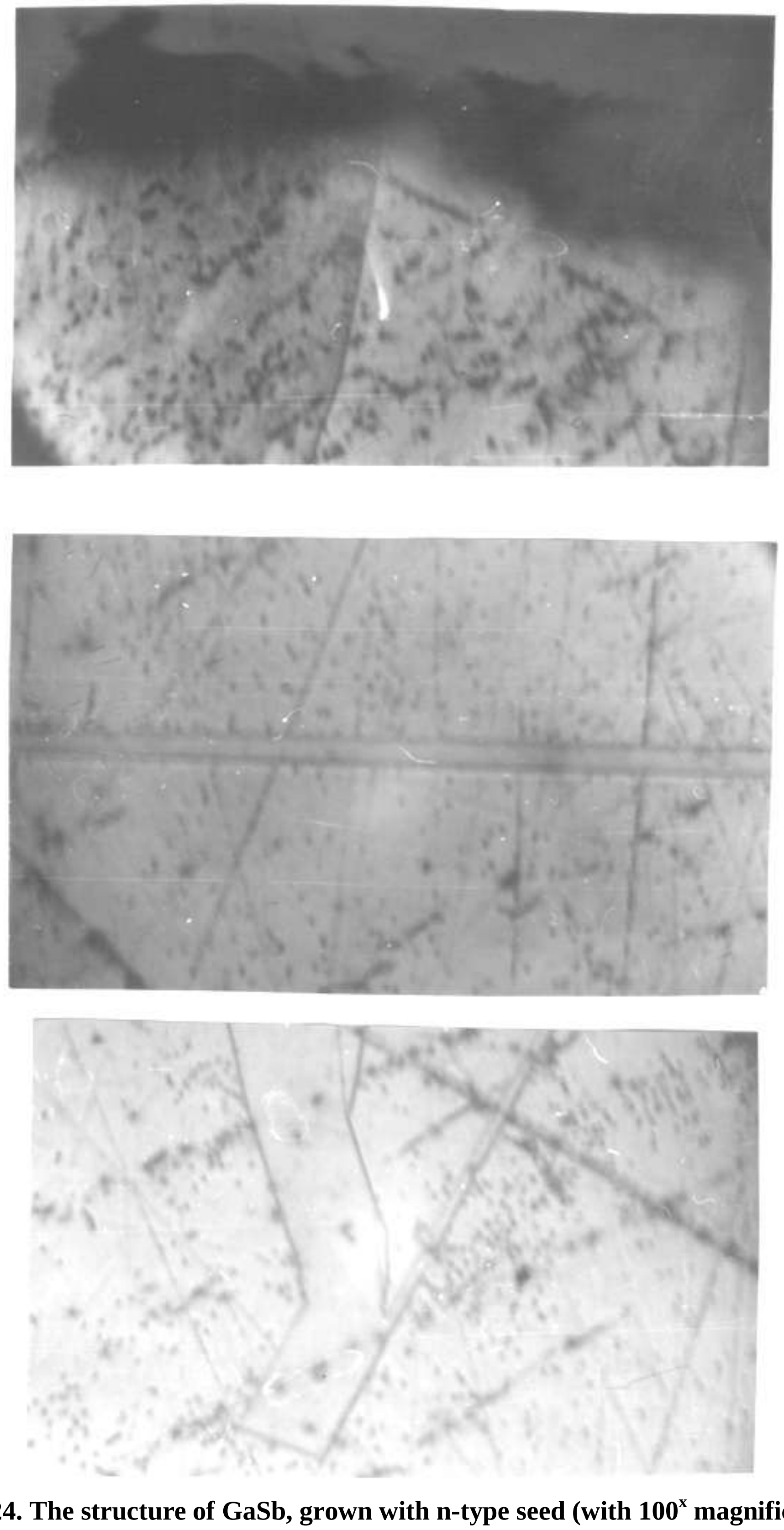

Figure 24. The structure of GaSb, grown with n-type seed (with 100^x magnification).

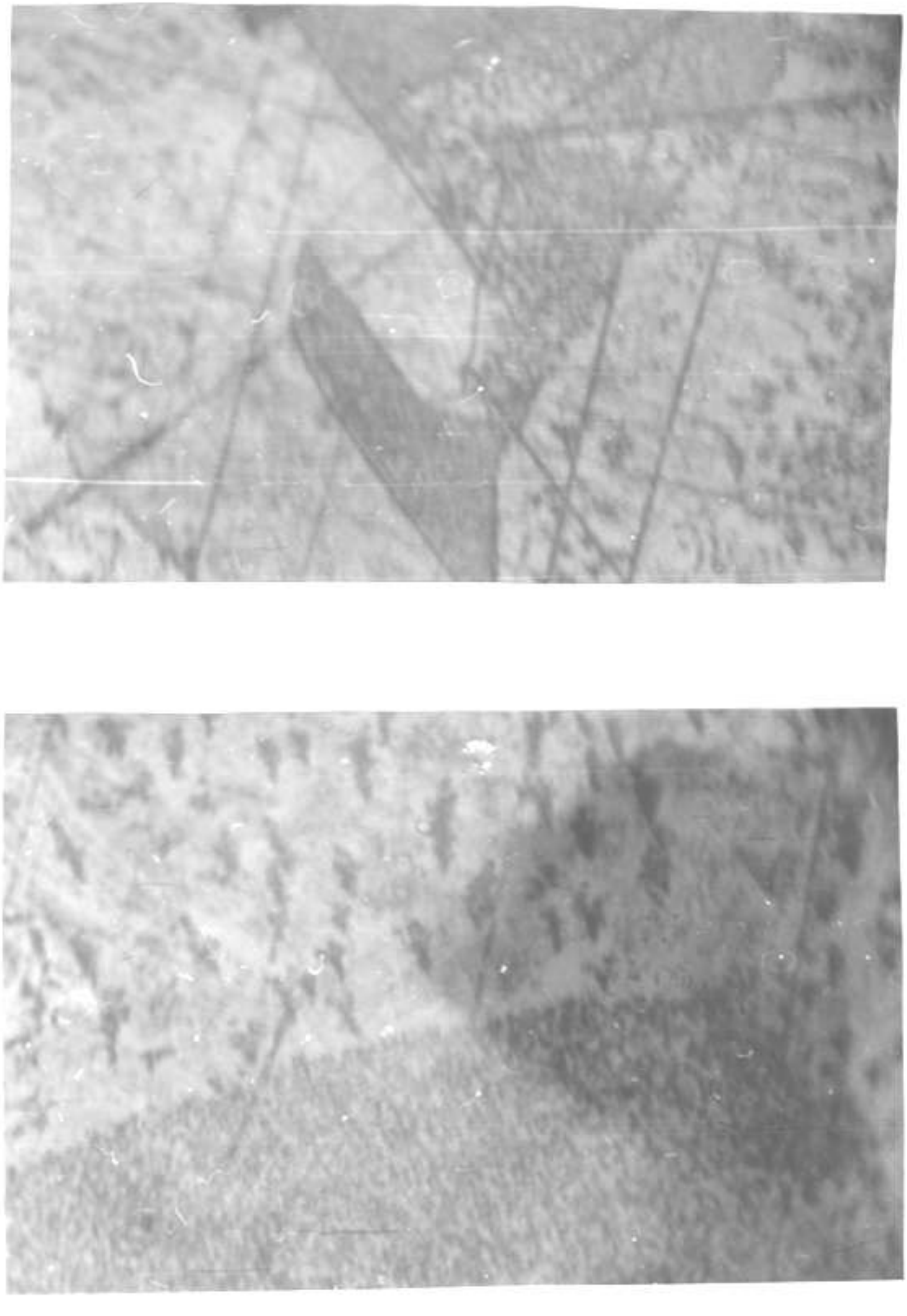

Figure 25a. The structure of GaSb, grown under MG condition (with 100^x magnification).

Figure 25b.The structure of cosmic crystal GaSb (with 100^x magnification).

References

REGEL L. L., Materials Science in space. Theory, Experiments, Technology
. (part 1), Halsted Press, NY (1986).

REGEL L. L., Materials Science in space. Theory, Experiments, Technology
. (part 2), Plenum Press, NY (1990).

CHERNOV A. A., In: Sbornik III Vsesojunii seminar po gidromekhanike I
. teplomassoobmenu v nevesomosti, Tezisi dokladov, Chernogolovka, 1984.

ZEMSKOV V. S. et al., The properties of GaSb-InSb crystals and solid
. solutions, doped with the elements of II, IV and VI groups. In: Sb. "Semi-
conductor's doping", Moscow, IMET (1982) pp. 77-81. (In Russian).

LENDVAN E. et al., Experiment "Etvish": Crystal growth under micro-
. gravity condition. In: Material science and technology, Moscow, Nauka (1985). (In
Russian).

LENDVAN E. et al., The structure biography of GaSb, growen under micro-
. gravity condition. In: Material science and technology, Moscow, Nauka (1985). (In
Russian).

SHOMODI K, and HEREH T., Some electro-physical properties of GaSb,
. growen under micro-gravity condition. In: Material science and technology,
Moscow, Nauka (1985). (In Russian).

NAGEL G, and BENZ K. Advanced Space Research, vol. 4, No. 5, pp. 23-26
. (1984).

BENZ K. et al., 6-th European Symposium on Material Science under Micro-
. gravity Condition, 1987, p. 345.

CHAORONG L. et al., An emulation for melting zone semiconductor single
0. crystal growth in space, Cryst. Res. Technol. Vol. 38, No. 7-8, pp. 734 – 739
(2003).