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Study of imperfect natural diamonds with the application of the X-ray synchrotron radiation (the "Laue-SR" method)

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Abstract

The "Laue-SR" method has been realised for fast gathering experimental data in the study of imperfect natural and synthesised diamonds which are hard to investigate with the conventional X-ray methods. Time to obtain a diffraction pattern with the use of the polychromatic SR is shorter by several orders; the resolution of the image of substructure defects of a crystal lattice (as compared to the conventional Laue method) is improved by an order and does not vanish even at large disorientation or other non-coherent disturbances of the crystal lattice. The "Laue-SR" method is especially appropriate for the study of intact, sufficiently large diamond crystals (up to 5 mm), since the diamond has a small coefficient of the X-ray absorption and is practically transparent in the operational range of the SR waves, λ =0.5–1.5 Å. This method was shown to be applied successfully for an accelerated study of a large bulk of imperfect natural diamond crystals without any preliminary preparation and without their destruction, which enlarges the information output in the study and, besides that, increases significantly the efficiency of the work. X-ray "Laue-SR" topograms of imperfect diamonds with different types of distortions of the crystal lattice by natural processes during the formation of the diamonds and by epigenetic impacts are shown. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A large part of the mined diamonds is referred to as imperfect crystals with bad optical and physical characteristics. A previous work [1] reports that as little as 15% of all diamonds that are mined at present can be referred to as jewellery ones.

Nevertheless, imperfect diamonds also carry significant information both on the structure of the crystals and on the abyssal processes in the Earth's mantle.

However, imperfect crystals drop out of the research to a large extent or are under-investigated.

This is linked with the specific physical-chemical properties of diamonds: the highest hardness

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(laboriousness of treatment), high fragility, high PT formation conditions, etc. Besides that, there are restrictions connected with the complication of the experimental conditions and lessening of the experimental variety when the crystals are, for instance, imperfect. This leads to difficulties in the use of the conventional X-ray methods, too.

At the same time, the synchrotron X-radiation exists and has been successfully used in different experiments for many years [2]. A synchrotron X-radiation source at BINP is at present the VEPP-3 storage ring. Application of a wiggler gives a possibility to increase the SR beam intensity by several orders, which allows observation of the diffraction pattern directly on the luminophor screen.

Since imperfect crystals have high density of crystallographic and other defects that are not resolvable even with high-resolution topographic methods, the objects of study in such crystals are substructure formations such as deformation bands and networks, areas of the lattice bend and reorientation, grain boundaries and fibres, regular and irrational twins, discharge bands and other non-coherent states of the crystal lattice.

Diamonds of $\sim$5 mm and less thickness are practically transparent for operational range of the SR wavelength $-\lambda = 0.5$–1.5 Å. Most samples under study are not more than 5 mm in thickness, therefore, there is a real possibility to investigate diamonds in the state they were formed in (by nature, for instance), without destruction or any other chemical-mechanical treatment.

To sum up, we can formulate the main reasons why the application of the "Laue-SR" method is more preferable for the investigation of imperfect diamond crystals:

1. Diamonds are transparent for SR in the working range of the X-radiation, $\lambda \sim 0.5$–1.5 Å; therefore, the survey of the diffraction patterns can be performed without destruction and treatment of the crystals, which expands the output of the useful information.
2. Samples are not to be treated mechanically to lessen their thickness (to meet the condition $\mu t \sim 1$), which increases significantly the work efficiency.
3. The high resolving ability of the "Laue-SR" method (because of the small divergence of the X-ray beam) allows, to a certain degree, a combination of the polychromatic Laue method and topography.
4. Reduction of the exposure time allows fast shooting in several crystal positions, which simplifies decoding of the diffraction patterns.
5. It is possible to use two-coordinate detectors or memory screens for automation of the studies.

2. Development of the method

The equipment that is applied for the "Laue-SR" method is very simple and is based on the idea of the X-ray chamber for the investigation of a fixed crystal (the Laue method). The difference from a conventional chamber is explained by the SR particularities, i.e. there is no usual collimator since the SR beam is weakly diverging, and the exposure is adjusted via additional attenuation of the diffracted radiation with the help of absorbers.

3. Description of the diamond crystals used for the study

The study was performed with about 30 crystals of natural diamonds. By some signs, it was possible to refer them to imperfect crystals. Below is presented a brief description of the most interesting crystals, whose sizes lay between 2 and 4 mm.

(a) Several crystals referred to the V-sort by the Orlov classification [3], of round habitus, dark, almost black because of a lot of black inclusions and micro-cracks.
(b) A round crystal (No. SK-36) with a lot of inclusions and cracks and slip traces on the surface. It can be referred to the "ballas" sort by its mineralogical characteristics.
(c) A popout from an MR-13 crystal, of almost isometric shape, up to 4 mm in size, with visual rough traces of plastic deformation on the surface, in the form of sub-parallel slip lines.

(d) Two mono-crystals of octahedral (No. V_n-97-15) and dodecahedral (No. BP-1/97) habitus, transparent, with visually observed rows of triangular pits caused by natural etching on the surfaces {1 1 1} of one of them, the rows passing throughout the crystal in parallel to the traces of the planes {1 1 1}.
(e) Two crystal wafers cut out from transparent octahedral crystals (from the Aikhal tube, the Yakut republic). By the data of double-refraction in polarised light, they have a mixed extinction pattern or that of the "tatami" type.
(f) Several crystals of cubic habitus (cuboids from Zaire, Africa) with a crystal edge size of 2 to 3 mm. They are opaque, with non-smooth surfaces {1 0 0}; etched channels (block or sector boundaries) are observed.

4. Results

The nature of imperfections of the interior substructure of diamonds may be caused by different factors.

At fast spontaneous growth under conditions of high oversaturation of the crystallisation medium, the crystals become block-like, cracked, with a quantity of trapped inclusions. Fibrous, spherulite-like diamonds, whose blocks are formations similar to fibres spreading from the crystal centre to the periphery, can be referred to such crystals.

Another reason for the appearance of imperfections is the plastic deformation that occurs after the initial formation of the crystal. It is possible that the crystal was relatively perfect before the deformation.

The variant when there were several stages of growth as well as subsequent post-growth transformations is also possible. In such a case, the nature of the imperfections will be combined, consisting of the growth and deformation phenomena. There appear blocks, bends, large rotation displacements, kinking, etc. in the crystals.

In other words, if fragmentation, asterism, diffuseness of the reflexes, etc. are present in the Laue pattern, the crystal is strongly deformed and further increase of the deforming load may cause fragile destruction. To describe the state of the sample's substructure objectively enough, one should analyse both the relevant Laue patterns and the interior structure of the spot-topograms (or their fragments), characterising the crystal structure particularities, which are linked, as a rule, with the initial formation processes and with the epigenetic deformations. Therefore, to illustrate the state of the interior substructure of the samples, we will cite the Laue patterns showing the general imperfection of crystals as well as separate spot-topograms characterising the structure particularities.

As it was mentioned above, diamond imperfection may be of the growth nature as well as of the post-growth (mainly deformation) one. The crystals that we studied can be divided into several groups by the results of the shooting by the "Laue-SR" method. Group I consists of several crystals that can be described as crystals that have undergone moderate plastic deformation. They look like well-faceted transparent crystals, which agrees with their mineralogical characteristics. Triangle pits by natural etching (sample Vn-97-15) are seen sometimes on their surfaces (facets) and a mixed extinction pattern of the "tatami" type (sample AC-155, AC-151) or long parallel dashes are seen in polarised light (sample BP-1/97).

The X-ray photos by the "Laue-SR" method are a clear evidence of a plastic deformation of these diamonds. Apparently, a high-temperature deformation occurred after the crystals formed as octahedrons, rhombododecahedrons and so on.

Fig. 1 shows one of several "Laue-SR" topograms with the diffraction image of two systems of deformation bands in the form of two lines crossing at an angle of $\sim 70°$. The lines bend at the edges of the topogram and then transform into thread-like "dabs", typical for crystals with asterism. Nevertheless, the Laue patterns from the crystals of group I correspond to normal crystals, i.e. they do not demonstrate typical asterism and fragmentation of the spot reflexes.

Another sort of deformation pattern is observed in the topograms of the sample BP-1/97. Only reflexes 2–4 of the Laue pattern have the interior

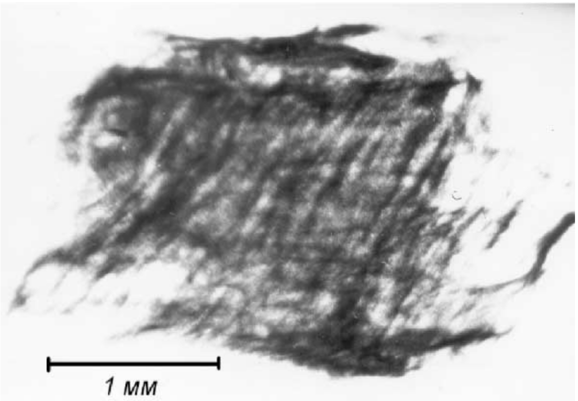

Fig. 1. One of the several "Laue-SR" topograms of a photograph with the diffraction image of two systems of deformation bands (sample Vn-97-15).

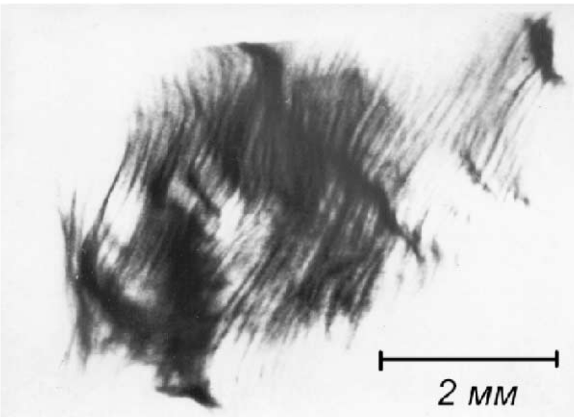

Fig. 2. A slip system's deformation bands throughout the crystal (sample BP-1/97).

structure in the form of wave bands passing through the spot. One slip system {1 1 1}-[1 1 0], obviously, was acting here (Fig. 2).

Two other samples of this group (wafers cut out of transparent octahedrons, the Aikhal tube, the Yakut republic) also have the Laue patterns of normal crystals. The spot structure also corresponds to a plastically deformed crystal lattice: the AC-155 sample contains deformation bands and other complex deformation contours and the "Laue-SR" topogram of the AC-151 sample shows the presence of small-angle deformation boundaries.

All the above-described crystals have normal Laue patterns (i.e. without asterism and fragmentation), but each of them has particular typical features of plastic deformation.

Less perfect samples, as expected, show a more intricate diffraction pattern.

The MR-13 sample is of the block structure and reflexes of its Laue pattern have a diffusive appearance and thread-like "dabs" at the edges. Both the diffraction effects, fragmentation and asterism, correspond to a significant plastic deformation; and the diffusive appearance of the spot topograms is, apparently, an evidence of multiple displacements of the crystal lattice areas in different directions.

Another kind of very imperfect natural crystals consists of diamonds of the V-sort [3]. The diffraction patterns show that the real structure of these crystals is a result of two particular processes: the imperfect growth, which led to the radial-ray fibre-like structure, and the superposed post-growth deformation. The presence of pronounced fragmentation and asterism effects testifies to a deep plastic deformation that occurred in the crystals. The imperfection of the substructure is confirmed by such facts as, for instance, one of the typical Laue patterns (Fig. 3) and structure of separate spot-topograms (Figs. 4–6).

Studying attentively such patterns from the V-sort series, one can assume that the crystals were in

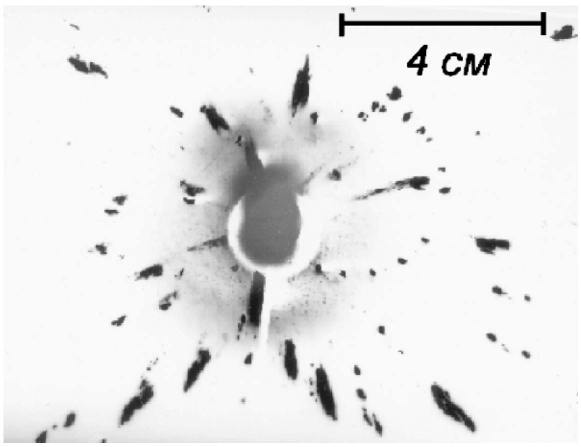

Fig. 3. A Laue pattern of the imperfect diamond R-100. Strong asterism and fragmentation of the spots.

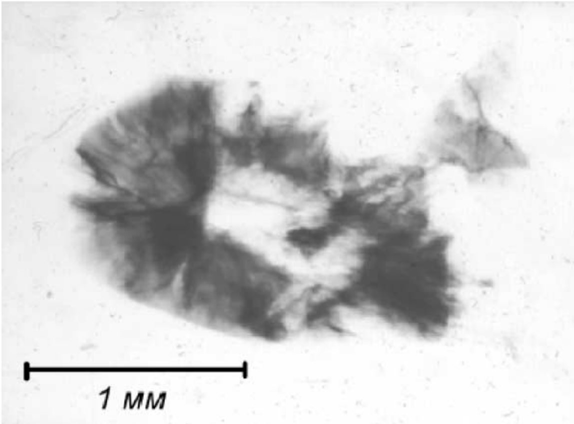

Fig. 4. Structure of the spot of the deformed diamond R-102.

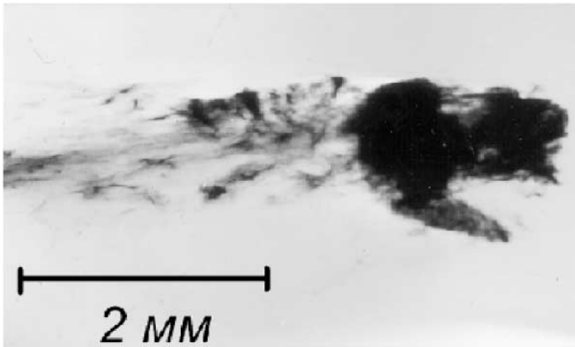

Fig. 5. Compact view of the spot-topograms of the R-101 sample.

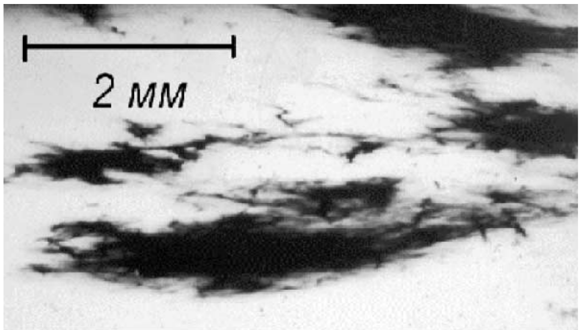

Fig. 6. Dendrite-like structure of a diamond of the V-sort.

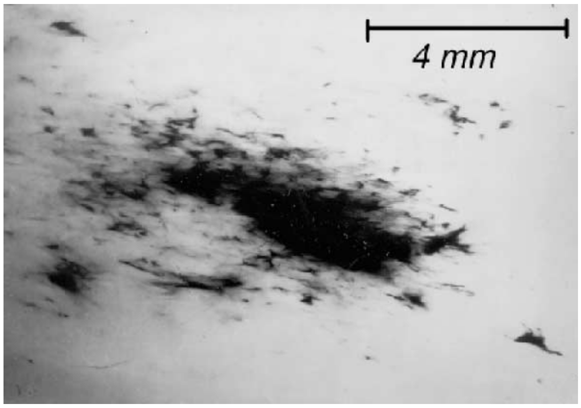

Fig. 7. Wide spots of the very imperfect sample SK-36 consist of a lot of reflexes of intricate form and size.

rather different conditions during their formation. Included among them there are crystals with a more perfect substructure (Fig. 4) and with a less perfect one, reminiscent of dendrites (Fig. 6).

The SK-36 sample sides to the same type of still more imperfect crystals. It is reminiscent of spherical diamonds of the ballas type by its mineralogical characteristic and X-ray diffraction pattern [3]. The spots in the Laue patterns of this crystal are a combination of small and larger points, dashes, junctions of short curves and so on, which occupy significant areas in the photograph (Fig. 7).

One more type of fibrous structure has cubic habitus crystals from Zaire (Africa). Among those investigated by the Laue-SR method are fine-fibred (Z-1, a Fig. 8a) and coarse-fibred (Z-2, Fig. 8b) samples.

The studies show that for such a type of substructures there is a tendency to undergo continuous transition from the structure elements in the form of fine fibres to coarser ones in other samples (Figs. 8a and b). The configuration of the coarse fibres becomes more intricate simultaneously, as if getting surrounded by shorter fibres. Finally, the whole substructure turns out to be a dendrite-like formation, whose skeleton comprises the "ray"-sectors of the crystal (sample Z-9, Fig. 8c). These ray sectors are surrounded by a ligature of wave fibres, whose X-ray image resembles like the sea foam network.

So, the samples studied are crystals of natural diamonds with different genetic origin of the

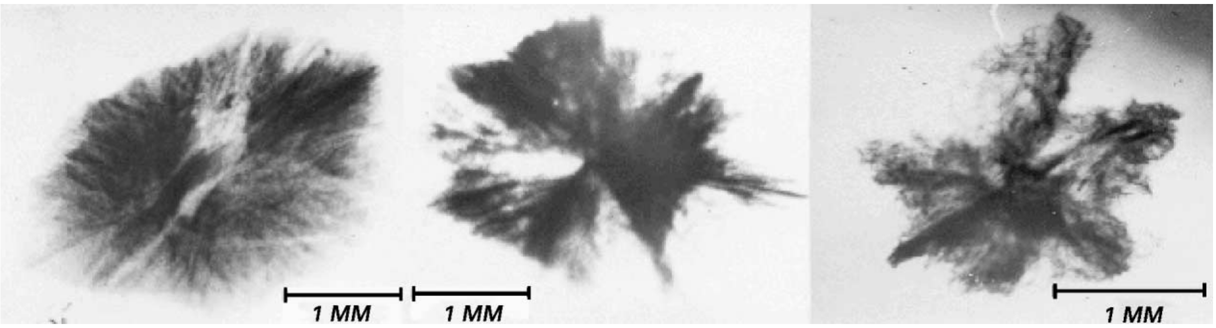

Fig. 8. A row of topograms of diamond cuboids to illustrate the fine-fibre (left, sample Z-1), coarse-fibre (centre, sample Z-2) and dendrite-like (right, sample Z-9) structure.

crystal lattice imperfections: deformation ones, with different degrees of plastic deformation, growth ones, with a fibrous radial-ray structure, and mixed ones, deformation-growth, arising when one process is superimposed over the other.

5. Discussion of the results

Imperfect natural diamonds, which make up more than 70% of the crystals mined at present, stand apart due to their extreme features, formation conditions and difficulty of study of non-treated crystals by some physical-chemical methods.

A series of samples with a moderate plastic deformation at our disposal (group I) is an evidence that there was a period when they were formed initially (it is possible that the crystals were almost perfect) and after that, at their further staying at rather high temperatures ($>1200^\circ$, [4,5]) in the Earth's mantle, the processes facilitating the deformation started [6]. The deforming loads, naturally, could be very different. This may explain the various substructure states of the crystal lattice of different samples. Nevertheless, no rough disturbances occurred and therefore no asterism or blocking phenomenon is observed in these crystals.

Another state of a crystal lattice is a stronger plastic deformation, which leads as in all crystal structures [7] to the phenomena of asterism at first and, later, of fragmentation of the spots in the Laue patterns. An example of such a state of reflexes is the diffraction patterns of the MR-13 sample, when the initial effects of a relatively strong plastic deformation are observed in the Laue patterns.

A greater deforming impact is noticed in the series of crystals of the V-sort, when the effects of strong asterism and significant fragmentation are observed in the diffraction patterns, which testifies to a strong deformation. We observe different degrees of distortion of the crystal lattice within this group of crystals and, maybe, different conditions of the initial formation (growth); for instance, different conditions of the oversaturation of the growth medium. The preferred substructure of these samples is a radial-ray fibre-like structure. We have observed such a structure of crystals with cubic habitus earlier [8].

Another ultimately imperfect crystal SK-36 can be an example of this tendency. It could be referred rather to the textured poly-crystals if the fine structure of the spots of its Laue pattern had not contained a dendrite-like structure. Since the dendrite branches can start at different points of the sample, the spots of the Laue pattern are a combination of minute points, dashes and junctions of short curves, reminiscent of a crystal split in a local volume (Fig. 9).

The phenomenon of the fibrous radial-ray growth of diamonds is seen rather clearly in the series of the eight studied cuboids from Zaire (Africa). Here we can see a regular row of crystals that can be described as fine-fibre (Fig. 8a), coarse-

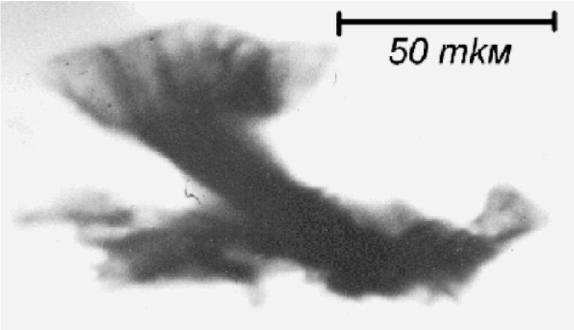

Fig. 9. "Splitting" in local volumes of crystals of the SK-36 type and V-sort of diamonds.

fibre (Fig. 8b) and dendrite-like (Fig. 8c) crystals with continuous transformations between them. In this example, one can see clearly that neither fibre structure nor even coarse dendrite structure leads to the phenomena of asterism and fragmentation in the Laue patterns. The presence of asterism and fragmentation and radial-ray structure in the samples of the V-sort is an evidence of different processes that run successively: at first, the crystals were "fibre-like" and then they became deformed at high temperature.

Since one can see a dislocation mechanism in all these transformations, it is possible to say that any imperfect diamond can be modelled via a combination of different types of dislocations (edge, screw, mixed, of particular type etc.). This lead to the genetic relationship of all types of split, fibrous, coarse-block, dendrite and so on crystals. Therefore, a continuous transformation between them is possible, which is verified by the experimental data of our work.

Several types of both deformation and growth substructures that are observed at the samples studied give an idea of the variety of the conditions of growth and epigenetic influence while crystals are deep in the Earth's mantle.

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