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# Raman scattering of impact diamonds



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### ABSTRACT

We report the results of a study of the polycrystalline powder of the diamond-lonsdaleite from the Popigai crater (Siberia) using UV micro-Raman spectroscopy and high-resolution synchrotron X-ray diffraction. By subtracting two experimental Raman spectra of diamond-lonsdaleite samples with close amounts of diamond and lonsdaleite, we were able to identify the polytypic composition of impact diamonds in contrast to the method of X-ray diffraction. We have managed to get for the first time the spectrum of "pure" lonsdaleite. Its deconvolution has allowed us to identify all the three Raman - active vibrational modes E2go, A1go, and E1g whose positions agree well with the results of ab initio calculations.

## 1. Introduction

Diamonds have a number of polytypes, of which lonsdaleite (also called hexagonal diamond, polytype 2H) has received particularly intense attention. Lonsdaleite was first described 50 years ago, as arose from the fall of an iron meteorite in the Canvon Diablo (Arizona, USA) [1]. Its formation was attributed to shock-induced transformation of graphite within the meteorite upon impact with the Earth. Lonsdale is given special attention due to its high mechanical properties, such as compressive strength, hardness and stiffness, which are comparable with the same properties of cubic diamond. However, these exceptional properties have not been proved experimentally due to the inability to find natural lonsdaleite in the form of a pure phase. In our opinion, at present, there are basically three self-consistent ways of interpreting the structure of lonsdaleite in impact diamonds.

1. The first way of interpreting is described in [2] in which it was shown by means of high-resolution electron microscopy that defects and twins in cubic diamond (polytype 3C) provide an explanation for the characteristic d-spacings and reflections reported for lonsdaleite. Therefore, the electron diffraction patterns originally classified as a hexagonal diamond, in fact, represent not a discrete material but faulted and twinned cubic diamond. The results of these studies raise doubts about the existence of lonsdaleite as a separate material and indicate that the layers of the lonsdaleite lattice can only arise as defects in the packing and twins in cubic diamond. These doubts about the existence of lonsdaleite, in general, were expressed because of the difficulties in creating a pure phase of lonsdaleite under static compression conditions. However, one must take into account that static compression is not well suited

to mimic the fast processes during impact events [3].

- 2. The second way to interpret the structure of lonsdaleite belongs to researchers from University College London [4,5]. They proposed a quantitative analysis of cubic and hexagonal stacking in diamond samples by analyzing the X-ray diffraction data with the DIFFaX software package (Diffracted Intensities from Faulted Xrystals). It was shown that the cubic and hexagonal sequences are interlaced in a complex way (e.g. ... chhcchchhchchcchc ...), which together may have, for example, trigonal symmetry. Thereby, naturally occurring lonsdaleite is not a simple physical mixture of cubic and hexagonal diamond. Instead, it is structurally best described as stacking disordered diamond. This means that the stacking errors interrupt the periodicity of the crystal in the direction of stacking, although the crystal can remain ordered in the other two dimensions. The characteristics of stacking disorder in diamond are conveniently summarized with a so-called stackogram, taking into account the effects of first order memory with two independent stacking probabilities.
- 3. In the third way of interpreting the structure of lonsdaleite, 3C and 2H polytypic structures may combine through a complex intermixture, which gives rise to other 2nH polytypes with larger-period stacking sequences [6,7]. For example, in work [8] in diamond nanoparticles polytypes 2H, 4H, 6H and thin layers (several atomic layers) of the hexagonal diamond were often observed with the help of transmission electron microscopy. The authors suppose that the formation of these polytypes and lonsdaleite layers is caused by the propagation and interaction of phonon waves in the crystal during high-temperature treatment when the phonon wavelength has the value of approximately several interplanar distances in the diamond lattice. Apparently, deformational twinning was also responsible for the formation of polytypes and lonsdaleite. In addition to thin

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layers, there were also observed the isolated lonsdaleite nanoparticles having a size up to nanometers. In other words, the number of polytypes, whose existence is possible for carbon diamond-like compounds, is practically unlimited. These polytypes share numerous crystallographic planes with the same *d*-spacings and their X-ray diffraction patterns are difficult to distinguish. Attempts at determining the polytypic composition by separating composite diffraction maxima into components do not make much sense and cannot serve as reliable evidence, since correct deconvolution into components requires taking into account the existence of not only the two main polytypes 2H and 3C, but also hundreds of other polytypes. In this case, the composite diffraction maxima can be separated in a hundred different ways within the same accuracy without a single-valued criterion for choosing the only correct variant of these separation methods. Thus, one cannot uniquely identify the polytype composition of the nanocrystalline impact diamonds with the help of electron diffraction patterns and X-ray diffraction patterns. Therefore, the goal of this work was an attempt to identify the polytype composition of nanocrystalline impact diamonds using Raman spectroscopy.

#### 2. Samples and experimental setup

We used impact diamonds from the Popigai impact crater with a diameter of  $\sim 100$  km located in the north of the Krasnoyarsk Territory produced by a meteorite impact about 35 million years ago. We studied the impact of diamond sampled from the tagamite (impact melt rock) that were collected from Skalnoe deposit (71° 30′19″ N, 110° 23′ 52″ E) inside the Popigai crater. This deposit is located in the middle of the crater (at a distance of about 20 km from the epicenter), in the region with the maximum content of carbonaceous rock and, accordingly, impact diamonds.

The Raman spectra of diamond and carbon materials are usually recorded under excitation by laser radiation with a wavelength in the visible or near-infrared region, which leads to a very high luminescence. Just like it was done in [9] we used UV excitation by a He-Cd laser with a wavelength of 325 nm, which allowed us to obtain the Raman spectra of diamond-lonsdaleite samples without any luminescence with narrower bandwidths. To avoid heating by laser beam, we used a low intensity, 1 mW, of the beam incident on the sample. For comparison, we additionally took the Raman spectra of the same samples with an ultralow radiation intensity of 0.1 mW, which turned out to be pairwise identical, without any frequency shift of the Raman bands of impact diamonds. These test measurements show no heating in the excitation zone of the Raman spectra. The Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR800 spectrometer with a 1024-pixel LN/CCD detector using an Olympus BX41 microscope [10]. The spectral resolution was approximately  $3.0 \text{ cm}^{-1}$  at a frequency shift of  $1300 \text{ cm}^{-1}$ . We used the PeakFit software package [11] to deconvolve the Raman spectra, which were represented as asymmetric Gaussian functions. It should be noted that the asymmetric approach to deconvolution of the vibrational spectrum of nanoparticles is justified and is widely used [12]. To make sure that lonsdaleite is present in our powders and to determine its percentage, we recorded the X-ray diffraction spectra. The X-ray diffraction patterns were recorded at the VEPP-3 storage ring station of the Synchrotron Center SSTRC at the Institute of Nuclear Physics, the Siberian Branch of the Russian Academy of Sciences. The wavelength of the synchrotron radiation is 0.3685 Å, the mean size of polycrystalline powder particles is 200 µm. A multichannel Image Plate MAR345 detector was used to record the diffraction. The intensity of diffraction rings was integrated by the FIT2D software [13]. The peaks of the measured X-ray diffraction patterns were analyzed by the method of decomposition into Voigt functions using Rietveld's method in the GSAS software package [14].



Fig. 1. The dependence of the diffraction peaks intensity on the amount of the lonsdaleite fraction in polycrystalline powders. A wavelength of synchrotron radiation  $\lambda = 0.3685$  Å.

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of a polycrystalline powder presented as the plots of the diffracted radiation intensity against the diffraction angle  $2\theta$ . Since, according to the previous measurements of X-ray diffraction in carbon impactites [15] and synthetic analogs [16], the contributions of hexagonal 2H and cubic 3C diamonds prevail among all of the sp3-polytypes, we consider our samples as a mixture of diamond and lonsdaleite. Then, we determine the lonsdaleite content in the two-component mixture from the intensity of diffraction peaks by using Rietveld's method and by taking into account the predominant orientation effect. We understand that this approximation of the estimation of the hexagonal component works only for mechanical mixtures, but at present, we are interested in the relative value, rather than the absolute value. The X-ray diffraction pattern presented in Fig. 1 shows a significant intensity of the lonsdaleite reflections (100)L and (101)L, which may be deemed the characteristic ones because they are located separately from the diamond reflections. Thus, lonsdaleite can be said to be present in our samples. The intensities of other lonsdaleite reflections located separately from the diamond peaks do not exceed the noise spikes, but Raman scattering is known to be more sensitive to structure crystallinity than X-ray diffraction. For example, in [17] as the pressure on crystalline Si increases to 10-12 GPa, the crystal peak on the X-ray diffraction pattern disappears, turning into a broad band of amorphous material, while this peak is retained in the Raman spectrum up to 15-17 GPa and completely disappears only at 19 GPa. Thus, it is hoped that the Raman scattering method will turn out to be more sensitive to the crystalline lonsdaleite component than X-ray diffraction.

In order to show that the use of laser excitation in the visible region



**Fig. 2.** Raman spectra of a polycrystalline diamond-lonsdaleite powder from the Popigai crater containing a different amounts of lonsdaleite. The lowest spectrum is recorded at laser excitation 325 nm, all others at laser excitation 514.5 nm.

of 514.5 nm leads to very high luminescence, we compare in Fig. 2 the Raman spectra with laser excitation in the visible region of 514.5 nm and in the ultraviolet region of 325 nm. The rising background in the 514.5 nm spectra is due to strong photoluminescence from nitrogenvacancy defects. Our diamond samples emit luminescence mainly in the region of yellow light (565–590 nm). Therefore, when we register the UV spectrum, we are much farther from the yellow photoluminescence region than when we register the Raman peak with excitation in the visible region. The result is that the UV spectrum is free from interference from the *PL* background, which is present when 514 nm excitation is used. This enables spectra to be collected at much a higher signal-to-noise ratio.

Fig. 3 presents the Raman spectra of "Popigai" impact diamonds with different lonsdaleite contents from 0 to 42% with laser excitation in the ultraviolet region of 325 nm. It can be seen from them that there is no signal at a frequency of  $1600 \text{ cm}^{-1}$  and, hence, there is no



Fig. 3. Raman spectra of a polycrystalline diamond-lonsdaleite powder from the Popigai crater containing a different amounts of lonsdaleite.



**Fig. 4.** An increase in the full widths at half maximums (FWHM) of the Raman spectra in Fig. 3, as a function of the lonsdaleite content.

graphite phase in our diamonds, only diamond and lonsdaleite are present. We assume that Popigai samples cover a wide range of impact effects, and it is expected that different levels of hexagonal and cubic stacking can be displayed not only in different samples, but even in the micro-nanoscale within this sample. We selected samples with a size of  $\sim$ 200 µm at different points of which we obtained approximately identical Raman spectra with a beam focusing of  $\sim 1 \,\mu m$ , *i.e.*, the samples were homogeneous. It can be seen from Fig. 3 that the spectra gradually broaden as the amount of lonsdaleite increases, slightly shift leftward, and a small feature at  $1215 \text{ cm}^{-1}$  appears in the sample with 18% lonsdaleite, which gradually increases. From Fig. 4 it can be seen that all points fit well approximately quadratically root dependence. Thus, it can be seen that when passing from sample to sample, there are no sharp jumps in diamond line width due to diamond defect density variations are observed, because we selected homogeneous samples. We should also take into account the fact that a high density of extended defects can lead to the effect of phonon confinement in the diamond crystal lattice, which lifts the ban on the manifestation of diamond phonon states from the low-frequency region in Raman scattering. Therefore, the maxima of the entire phonon density of states of the diamond in the Brillouin zone can manifest themselves in the spectrum [18]. To get rid of the contribution of the cubic diamond, it should be subtracted from our spectrum. Thus, for the time being, we assume that the polycrystalline diamond-lonsdaleite powder from the Popigai crater is a simple physical mixture of cubic and hexagonal diamond. Then, in conclusion, we will explain the validity of this assumption.

It is difficult to obtain an accurate Raman spectrum of lonsdaleite by subtracting the diamond spectrum from the Raman spectrum of mixed diamond-lonsdaleite samples due to the great uncertainty in the width and position of the diamond band. Since, as we have mentioned above, lonsdaleite is structurally best described as the stacking of disordered diamond, the diamond band in the Raman spectrum of mixed diamondlonsdaleite samples broadens greatly and shifts with increasing lonsdaleite content. Obviously, to obtain the smallest uncertainty, it is necessary to subtract two experimental Raman spectra with different, but close ratios of the diamond and lonsdaleite fractions in order for the diamond line width to remain practically the same. Fortunately, we found two samples with close lonsdaleite content of 25 and 32%. When we equated the amplitudes of their Raman spectra (see Fig. 5), it became clear that their right sides are the same, which means that the width of the diamond peak remained almost the same. The maximum contribution to the difference spectrum must then be associated with the difference of the lonsdaleite contributions and not with the change in the diamond band width due to defects. As was pointed out previously in our paper [19], the intensity of the Raman spectra for



**Fig. 5.** The two experimental Raman spectra of samples containing different ratios of the diamond and lonsdaleite fractions are presented at the top. The red and black spectra contain 32% and 25% of lonsdaleite, respectively. Four difference spectra obtained when the spectrum being subtracted with a smaller lonsdaleite content was multiplied by k = 0.68 (1), 0.85 (2), 0.93 (3), and 1 (4) are presented at the bottom. The dotted line shows the magnitude of the asymmetry of the peaks. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diamond-lonsdaleite samples is proportional to the percentage of cubic diamond. Since the spectrum being subtracted contains more cubic diamond, it should be multiplied by different coefficients k < 1. We multiplied it by 0.68, 0.85, 0.93, and 1 to minimize the contribution of the diamond spectrum (Fig. 5, four spectra at the bottom). At k = 0.85the main band of the difference spectrum narrows down sharply, because the broadening caused by the splitting of the main bands of lonsdaleite at  $\approx 1300 \text{ cm}^{-1}$  and diamond at  $\approx 1332 \text{ cm}^{-1}$  in the impact mixture vanishes due to the disappearance of the diamond contribution. Therefore, spectrum (2) with k = 0.85 seems the best one. It should be remembered that if low-frequency maxima of the phonon density of states in the Brillouin zone were present in the cubic-diamond spectrum, then they were also removed during the subtraction. Therefore, the difference in the spectra with high accuracy represents an additional structure without the contribution of 3C diamond. Which of the three ways described in the introduction should be chosen to identify this lonsdaleite structure, represented by the spectrum (2) in Fig. 5, we do not yet know. This additional structure can accordingly be the total contribution either from the defects in the packing of cubic diamond, or from polytypes with a stacking disorder in diamond, or from a complex mixture of 2nH polytypes, which includes lonsdaleite.

Let's first we assume that the additional structure is due to the total contribution from the polytypes with a random packing order of cubic and hexagonal layers in one direction, which together possesses neither cubic nor hexagonal symmetry and do not represent a simple physical mixture of them. In this case, in the samples with increasing concentration of lonsdaleite, structures with different Raman spectra and with different symmetries should form, which will lead to arbitrary shifts of the total Raman spectrum, which contradicts the experiment. Moreover, these structures will have approximately the same amplitude. However, Fig. 3 shows that with an increase in the contribution of lonsdaleite, the additional structure monotonically increases and the spectra asymmetrically broaden, indicating an increase in the contribution of a single-type structure with a definite symmetry. It should



**Fig. 6.** (a) The experimental difference Raman spectrum (2) of lonsdaleite taken from Fig. 5 (blue dots). (b) The three Raman-active vibrational modes  $E_{2g}$ ,  $A_{1g}$ , and  $E_{1g}$  obtained *via* deconvolution from the upper spectrum whose <u>ag</u><u>regated</u> spectrum is indicated by the red line on the upper spectrum. (c) The theoretical Raman spectrum of lonsdaleite obtained through *ab initio* calculations by taking into account the Lorentzian profiles of the peaks with a full width at half maximum of 10 cm<sup>-1</sup> [4]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also be taken into account that we are investigating a polycrystalline powder when the Raman spectra for all directions are averaging.

In this case, it turns out that the additional structure, represented by the spectrum (2) in Fig. 5, is described either in a first way, that is, by the contribution from the defects of the packing of the cubic diamond, or by a third way, that is, by the contribution from a complex mixture of 2nH polytypes. To determine the kind of this additional structure, it is necessary to carry out its deconvolution with the aid of asymmetric Gaussian profiles. Fig. 6 shows that after deconvolution, we managed to extract all three Raman-active vibrational optical modes whose positions agree well with the results of ab initio calculations from [4]. The ab initio calculations of the Raman spectrum for lonsdaleite were performed using a hybrid functional because these functionals provide a very high accuracy in reproducing the vibrational properties of crystals. In particular, the Lee-Yang-Parr exchange-correlation functional mixed with 16% of the Hartree-Fock exchange [20] was used here. According to the ab initio calculations, the most intense band in the experimental Raman spectrum at 1305 cm<sup>-1</sup> was attributed to the longitudinal optical vibrational mode  $A_{1g}$ , while the other two bands at 1244 and  $1356 \text{ cm}^{-1}$  were attributed to the transverse optical vibrational modes  $E_{2g}$  and  $E_{1g}$ . These bands are highly broadened  $(50-60 \text{ cm}^{-1})$  and slightly  $(\sim 10 \text{ cm}^{-1})$  shifted toward low energies due to lonsdaleite imperfection.

Thus, it turns out that the additional structure is due to the contribution of only one hexagonal component, by the lonsdaleite. Fig. 3 shows that with an increase in the content of lonsdaleite to only 4%, the half-width of the Raman peak increases almost threefold to  $30 \text{ cm}^{-1}$ , that is, the defectiveness of a cubic diamond greatly increases. Suppose



**Fig. 7.** The two experimental Raman spectra of samples containing different ratios of the diamond and lonsdaleite fractions are presented at the top. The black and red spectra contain 75% and 68% of cubic diamond, respectively. Three difference spectra obtained when the spectrum being subtracted with a smaller diamond content was multiplied by k = 0.80 (1), 0.85 (2), and 0.90 (3) are presented at the bottom. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 8.** Comparison of two spectra of cubic diamond. Above is the difference spectrum (2) of Fig. 7 with the half-width of the line is  $40 \text{ cm}^{-1}$ , below is the spectrum of the impact diamond not containing lonsdaleite from Fig. 3 with a half-width of the line of  $10 \text{ cm}^{-1}$ .

first that under the influence of temperature and pressure on the layers of diamond there heterogeneously crystallize and grow layers of lonsdaleite as described in methods 2 and 3 in the introduction. The addition of only 4 layers of lonsdaleite to 96 layers of cubic diamond cannot cause such a strong change in the structure of cubic diamond, which will lead to an increase in the half-width of the Raman peak by a factor of three. But it makes difference, if we get lonsdaleite not by growth and crystallization, but by deforming a cubic diamond. In this case, the deformation can be quite significant, until 4% of the diamond does not change its *d*-intervals to values characteristic of lonsdaleite as described in the first way in the introduction. This remark serves as an additional argument in favor of the fact that the additional structure is described in a first way, that is, by the contribution from the defects of the packing of the cubic diamond. From what was said above, it turns out that from the experimental Raman spectrum of the diamond-lonsdaleite sample, it is possible to extract the Raman spectrum of the lonsdaleite, that is, the impact diamonds from the Popigai impact crater can be considered as a simple physical mixture of cubic and hexagonal diamond.

In order to fully identify the polytypic composition of nanocrystalline impact diamonds, it is necessary to obtain the Raman spectrum of a "pure" diamond in a similar manner, by subtracting the spectrum of the lonsdaleite from the Raman spectra of the diamond-lonsdaleite samples. We use the same Raman spectra as in Fig. 5, only now we to equalize the lower parts of the spectra in amplitude, which determine the amount of the lonsdaleite. Fig. 7 shows that the Raman spectra practically coincided, except for the diamond peaks, that is, the difference spectrum should be related only to the difference in the contributions of the cubic diamond. Now, from the spectrum of the sample containing 75% of cubic diamond, the spectrum of the sample with 68% of cubic diamond is subtracted. Since the spectrum being subtracted contains more lonsdaleite, it should be multiplied by different coefficients k < 1. We multiplied it by 0.80, 0.85 and 0.90 to minimize the contribution of the lonsdaleite spectrum (Fig. 6, three spectra at the bottom). The spectrum (2) turned out the most suitable. Fig. 8 shows for comparison two spectra of cubic diamond, the difference spectrum 2 from Fig. 7 with the half-width of the line  $40 \text{ cm}^{-1}$  and the spectrum of the impact diamond not containing lonsdaleite from Fig. 3 with a halfwidth of the line of  $10 \text{ cm}^{-1}$ . It turns out that in an impact diamond that contains ~30% of lonsdaleite, the diamond band of cubic diamond 3C is broadened 4 times and does not shift in energy with increasing content of lonsdaleite, which means that there is no compressive or tensile stress in the samples.

# 4. Conclusion

Investigating the shape of the experimental Raman spectra, we showed that the structure of lonsdaleite in impact diamonds is best interpreted by the first way indicated in the introduction, *i.e.*, the layers of the lonsdaleite lattice can only arise as defects in the packing and twins in cubic diamond, as described in [2]. It turned out that the second way, characterizing the stacking disorder of cubic and hexagonal layers, is not very suitable for describing the structure of lonsdaleite in impact diamonds. This way works well in describing the crystallization of ice after homogeneous nucleation from drops of pure water at atmospheric pressure [21]. Perhaps this is due to the fact that in our case the process of nucleation of lonsdaleite is of a highly heterogeneous character. Since a defect cubic diamond is first formed from graphite, without the formation of lonsdaleite, the Raman spectrum of which has a half-width of  $10 \text{ cm}^{-1}$ . Secondly, anisotropic deformations, during shock events, can make ambiguous the results of the crystal nucleation of hexagonal atomic layers. And thirdly, this theory does not take into account the very large increase in the broadening of the Raman spectra, which is inextricably linked with the increase in the amount of lonsdaleite.

In conclusion, we were able to identify the polytypic composition of impact diamonds using *UV* micro-Raman spectroscopy in contrast to the *X*-ray diffraction method.

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