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ATOMS, MOLECULES, = OPTICS

Raman Scattering in Lonsdaleite

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Abstract—We present the results of our study of a polycrystalline diamond–lonsdaleite powder from the Popigai crater (Siberia) using UV micro-Raman scattering and synchrotron X-ray diffraction. By subtracting two experimental Raman spectra of diamond–lonsdaleite samples with a close ratio of the diamond and lonsdaleite fractions, when the maximum contribution to the difference spectrum is related to the difference of the lonsdaleite contributions and not to the change in the diamond band width, we have managed to obtain the spectrum of "pure" lonsdaleite. Its deconvolution has allowed us to identify all three Raman-active vibrational modes E_{2g} , A_{1g} , and E_{1g} whose positions agree well with the results of *ab initio* calculations.

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1. INTRODUCTION

Diamond has a number of polytypes, of which lonsdaleite (also called hexagonal diamond, the 2H polytype) has received particularly intense attention. Lonsdaleite was first described almost 50 years ago from the Canyon Diablo iron meteorite (Arizona, USA) [1]. Its formation was attributed to shockinduced transformation of graphite within the meteorite upon impact with the Earth. Such impact diamonds are polycrystalline aggregates composed predominantly of cubic and hexagonal diamond nanoparticles and residual crystalline graphite [2]. Lonsdaleite has received much attention because of its superior mechanical properties, such as compressive strength, hardness, and rigidity, thought to rival or exceed those of cubic diamond. However, these exceptional properties have not been proven experimentally because of the inability to synthesize lonsdaleite as a pure phase. In [3] it is pointed out that 2H polytypes cannot be formed due to the absence of strict ordering of layers in the original graphite that experiences inhomogeneous stresses under impacts. As a result, the forming diamond contains an enormous number of stacking faults; therefore, the materials termed lonsdaleite are defect diamonds with a random layer stacking order. 2H polytypes with an ideal structure can be obtained only during epitaxial growth of diamond crystals on a substrate with a certain morphology [4]. However, this mechanism cannot be realized during the formation of diamond-like materials at meteorite fall sites. Simulations of the conditions under which the 2H polytype of diamond is formed from graphite have shown that this process is possible as a result of static graphite compression at high pressures [5]. In all these cases, the product being synthesized also contains cubic diamond, graphite or both. Diamond crystals with a random stacking of layers will be formed under impacts on graphite, and a pure 2H polytype cannot be obtained in this way. Hence, it can be said that, from a crystallographic point of view, lonsdaleite is a defect diamond with a random stacking of layers differing not only by the order of their alternation, but also by hexagonality. Therefore, the most intense diffraction peaks on the X-ray diffraction patterns are located at close diffraction angles. As a result, for nanocrystalline samples these peaks are strongly smeared and combined diffraction peaks are formed when they overlap, so that the final X-ray diffraction pattern becomes similar to that of other polytypes, primarily the 3C polytype. Thus, the polytype composition cannot be unambiguously identified for nanocrystalline diamonds. As a result, very wide overlapping Raman spectra of these carbon agglomerates that cannot be unambiguously interpreted are generally presented in the literature. In addition, the paper [6] has recently appeared, where defects and twins in cubic diamond are shown to provide an explanation for the characteristic *d*-spacings and reflections reported for lonsdaleite using a high-resolution electron microscope. These findings question the existence of lonsdaleite and point to the need for reevaluating the interpretations of many lonsdaleite-related publications.



Fig. 1. (Color online) The X-ray diffraction pattern of a polycrystalline powder from the Popigai impact crater recorded using synchrotron radiation with a wavelength $\lambda = 0.3685$ Å. The scale of interplanar spacings *d* corresponding to a diffraction angle 20 according to the Bragg formula $2d\sin\theta = n\lambda$, where λ is the wavelength of monochromatic X-ray radiation and *n* is the order of reflection from the crystal plane, is shown at the top. In this powder the lonsdaleite content determined by Rietveld's method is 49%.

2. THE SAMPLES AND THE EXPERIMENTAL SETUP

The goal of this paper was to obtain such a Raman spectrum of an impact diamond with a random stacking of layers differing not only by the order of their alternation, but also by hexagonality that would allow traces of defect lonsdaleite to be found. We used impact diamonds from the Popigai impact crater with a diameter of ~100 km located in the north of the Krasnovarsk Territory produced by a meteoritic impact about 35 million years ago. 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 range, which leads to a very high luminescence. 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 bands. To avoid the heating by the laser beam, we used a low intensity, 1 mW, of the radiation 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 [7]. The spectral resolution was approximately 3.0 cm^{-1} at a frequency shift of 1300 cm^{-1} . We used the PeakFit software package [8] to deconvolve the Raman spectra, which were represented as asymmetric Gaussian functions. It should be noted that the asymmetric approach to deconvolving the vibrational spectrum of nanoparticles is justified and is widely used [9]. 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 [10]. 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 [11].

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of a polycrystalline powder presented as a plot of the diffracted radiation intensity against the diffraction angle 2θ . Since, according to the previous measurements of X-ray diffraction in carbon impactites [12] and synthetic analogs [13], the contributions of hexagonal 2H and cubic 3C diamonds prevail among all of the sp^3 -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. 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 two other lonsdaleite reflections, (102)L and (103)L, 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 [14] 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.



Fig. 2. (Color online) Raman spectra of a polycrystalline diamond–lonsdaleite powder samples from the Popigai crater containing different amounts of lonsdaleite. The lowermost spectrum of natural diamond from kimberlites is presented for comparison.

Figure 2 presents the Raman spectra of our samples with different lonsdaleite contents from 0 to 42%. It can be seen from them that there is no signal at a frequency of 1600 cm^{-1} and, hence, there is no graphite phase in our diamonds, only diamond and lonsdaleite are present. We selected samples with a size of $\sim 200 \,\mu\text{m}$ 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. 2 that the spectra gradually broaden as the amount of lonsdaleite increases, slightly shift leftward, and a small feature at 1215 cm⁻¹ appears in 18% lonsdaleite, which gradually increases. Thus, it can be seen that when passing from sample to sample, no scatters 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 [15]. To get rid of the contribution of the cubic diamond, it should be subtracted from our spectrum.

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 a defect diamond with a random stacking of layers, the diamond band in the Raman spectrum of mixed diamond—lonsdaleite samples broadens greatly and shifts with increasing



Fig. 3. (Color online) 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.

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 as before. Here, the spectrum of a sample with a 25% lonsdaleite content is subtracted from the spectrum of a sample with a 32%content; in this case, it can be seen from Fig. 3 that the right sides of the bands coincide. 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 [16], the intensity of the Raman spectra for 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. 3, four spectra at the bottom). At k = 0.85 the 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 ≈ 1332 cm⁻¹ in the impact mixture van-



Fig. 4. (Color online) (a) The experimental difference Raman spectrum 2 of lonsdaleite taken from Fig. 3 (blue dots). (b) The three Raman-active vibrational modes E_{2g} , A_{1g} , and E_{1g} obtained via deconvolution from the upper spectrum whose combined 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⁻¹ [17].

ishes 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, we think that the maximum contribution to the difference spectrum must be associated with the difference of the lonsdaleite contributions.

Then, from this spectrum, which represents the contribution of about 7% of "pure" lonsdaleite, we managed to extract all three Raman-active vibrational optical modes using the deconvolution of asymmetric Gaussian profiles; their positions agree well with the results of *ab initio* calculations from [17] (Fig. 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 [18] was used here.

According to the ab initio calculations, the most intense band in the experimental Raman spectrum at 1305 cm⁻¹ was attributed to the longitudinal optical vibrational mode A_{1g} , while the other two bands at 1244 and 1356 cm⁻¹ were attributed to the transverse optical vibrational modes E_{2g} and E_{1g} . These bands are highly broadened (50–60 cm⁻¹) and slightly (~10 cm⁻¹) shifted toward low energies due to lonsdaleite imperfection.

4. CONCLUSIONS

According to present views [3, 19], the 3C and 2H structures can combine through a complex intermediate mixture that gives rise to other 2nH polytypes with stacking sequences with a large period. However, despite the fact that the 3C and 2nH polytypes have a lot of crystallographic planes with identical spacings d and their X-ray diffraction patterns are difficult to distinguish, the Raman spectrum shows all the allowed optical phonons of the hexagonal Brillouin zone, suggesting the presence of extended hexagonal stacking sequences in our natural samples. In other words, the final Raman spectrum is a broadened spectrum of the 2H polytype obtained through ab initio calculations.

Thus, we think that UV micro-Raman scattering can be applied to diagnose such polytypic cubic—hexagonal structures. Diffraction investigations were supported by the Ministry of Education and Science of the Russian Federation (project no. RFMEFI62117X0012).

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