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## Experimental Investigation of the Linear and Nonlinear Elastic Properties of Synthetic Diamond Single Crystal

**Boris P. Sorokin\***

**Gennady M. Kvashnin**

**Mikhail S. Kuznetsov**

Technological Institute for Superhard and Novel Carbon Materials,  
Central'naya, 7a, Troitsk, Moscow, 142190

Russia

**Arseny V. Telichko<sup>†</sup>**

Moscow Institute of Physics and Technology,  
Institutsky Lane, 9, Dolgoprudny, Moscow Region, 141700

Russia

**Sergey I. Burkov<sup>‡</sup>**

Institute of Engineering Physics and Radio Electronics,  
Siberian Federal University,  
Svobodny, 79, Krasnoyarsk, 660041

Russia

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*Experimental results of the propagation of bulk acoustic waves (10–200 MHz) in the synthetic diamond single crystal under the influence of uniaxial pressure and temperature have been presented. Obtained data of the second and the third order of elastic constants were used for calculation of the anisotropy of the acoustic waves propagation characteristics in diamond under the pressure application. The peculiarities of wave propagation have been discussed*

*Keywords: bulk acoustic wave, uniaxial pressure, temperature influence, synthetic diamond, second- and third-order elastic constants*

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## Introduction

Large good quality natural single crystals of diamond are very rare, they have the great cost and therefore cannot be regarded as an important source of raw materials in such that high technology areas as optics and electronics. Nevertheless, diamond single crystal has a number of unique properties and characteristics which has the interest for its potential application in acoustoelectronics: the highest among the known solids bulk (BAW) and surface (SAW) acoustic wave velocities, high thermal conductivity, ionizing radiation stability, chemical resistance, and so on. Physical properties of diamond have the great importance in terms of solid state studies and, in recent years, owing to the applied applications of diamond films and single crystals. The measurements of elastic moduli (second-order elastic constants (SOEC)) and its temperature

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\*bpsorokin2@rambler.ru

<sup>†</sup>arseny.telichko@phystech.edu

<sup>‡</sup>sburkov@sfu-kras.ru

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and pressure dependences for natural diamond with a good accuracy have been executed by the authors [1], who have developed the high-frequency ultrasound long pulse method, suitable for samples with small geometric dimensions. But third order elastic constants (TOEC) hadn't been defined. Indirect methods, such as *X*-ray diffuse scattering [2] and Brillouin scattering [3], have also been used to determine the second-order elastic moduli of diamond. Recent measurement of the diamond's elastic moduli was executed by the method of resonant ultrasound spectroscopy [4].

To analyze the SOEC dependence of the temperature or pressure it is necessary to know the full set of TOEC coefficients. The TOEC's for diamond have been theoretically obtained by *ab initio* calculation, using the method of local electron density functional [5], and on the basis of linear and nonlinear force constants, calculated according to the Keating's theory [6]. By measurement of Raman shifts of optical phonons with uniaxial stress authors [7] have obtained the Keating's anharmonic parameters of the valence-force-field model as well as the diamond's TOEC values. In addition, the experimental TOEC values were found by the method of shock-wave loading [8].

During the last 3–4 years Technological Institute for Superhard and Novel Carbon Materials (Russia) began the production of sufficiently large samples of synthetic dielectric diamond with linear dimensions up to 10 mm in reproducible quality. The aims of this study were the measurements of the BAW velocities, including the investigations of uniaxial pressure and temperature influences, calculation of the second and third order elastic constants and anisotropy of BAW propagation parameters in synthetic dielectric diamond single crystal (type IIa with low nitrogen content  $< 2 \cdot 10^{16} \text{ cm}^{-3}$ ) under the action of uniaxial pressure.

## Experiment

Diamond single crystal specimens with the [110] and [001] crystalline faces oriented to within  $5'$  were prepared with a nonparallelism of opposite faces up to  $1 \text{ } \mu\text{m}/\text{cm}$  and a flatness better than  $\pm 100 \text{ nm}/\text{cm}$ . BAW phase velocities were measured by the interferometer pulse-phase method like [1], realized by Ritec Advanced System RAM-5000 in the frequency range 10–200 MHz. Piezoelectric quartz transducers with fundamental frequencies of 12 MHz for longitudinal (*L*) and 18 MHz for shear (*S*) waves have been used. The measurements were performed on the harmonics transducers up to 200 MHz. Epoxy resin's acoustic contact between the sample and fused silica buffer has been used. Since there was difficult to determine the layer thickness of an acoustic contact, a special method to minimize its influence has been used. High frequency measurements should also to minimize the dispersion errors due to diffraction effects and the acoustic wave's reflections on the side walls of the sample. Taking into account the phase error and sample preparation's inaccuracy, the phase velocity experimental error has been estimated as  $\pm 0.05 \%$ . Pure acoustic modes have been investigated only.

When the measurements of BAW velocities dependences on the uniaxial pressure *P* have been performed, the scheme of echo pulse measurement without buffers has been used. Pressure up to 30 MPa was produced by the Instron 5965 automatic electromechanical system with inaccuracy of the measurement up to 5%. The BAW's phase velocity variations, arising under the influence of uniaxial pressure on diamond single crystal, were measured by the time shifting of one of reflected acoustic pulses. More accurate and reproducible results can be obtained only if the median region of pulse was taken into account to measure the required time shift. The limiting time resolution was close to 20 picosecond. The pulse has been chosen as far as from the exciting one to obtain the best sensitivity. All the  $v = f(P)$  dependences were the linear ones. Temperature dependences,

investigated within the  $-60 \dots +70^\circ\text{C}$ , were observed the linear ones too.

## Calculation of Second- and Third-order Elastic Constants of Diamond

Well-known equations obtaining for the 3 independent second-order elastic coefficients  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  of cubic symmetry crystals with BAW phase velocities are given in the Tab. 1. Under the calculation of the  $C_{ij}$  coefficients the density value  $\rho_0=3516 \text{ kg/m}^3$ , obtained by measurement of unit cell parameter [9], has been used. The SOEC values of synthetic diamond at room temperature are presented in the Tab. 2 in comparison with known data. Taking into account the effect linear thermal dilatation [10] and  $v = f(T)$  dependences, the SOEC temperature coefficients have been calculated too (Tab. 2). Since the phase velocity variations are proportional to the pressure it is convenient to introduce controlling coefficients

$$\alpha_v = \frac{1}{v(0)} \left( \frac{\Delta v}{\Delta P} \right)_{\Delta P \rightarrow 0}. \quad (1)$$

Table 1. BAW velocities of diamond single crystal (type IIA) at room temperature

Propagation direction $N$	Polarization $U$	BAW's type	$\rho_0 v^2$	Phase velocity, m/s
[100]	[100]	$L$	$C_{11}$	$17542 \pm 1$
[100]	$\perp(100)$	$S$	$C_{44}$	$12828 \pm 1$
[110]	[110]	$L$	$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	$18333 \pm 1$
[110]	[001]	$S_1$	$C_{44}$	$12829 \pm 1$
[110]	$[\bar{1}\bar{1}0]$	$S_2$	$\frac{1}{2}(C_{11} - C_{12})$	$11659 \pm 1$

Table 2. Elastic moduli  $C_{IJ}$ (GPa) of diamond and its temperature coefficients at room temperature in comparison with previous data

	[1]	[3]	[4]	This work	
$C_{11}$	1079	1080.4	1078.16	$1081.9 \pm 1.0$	
$C_{12}$	124	127.0	126.63	$125.2 \pm 0.8$	
$C_{44}$	578	576.6	577.56	$578.6 \pm 0.2$	
				Experiment	Theory
$TC_{11}$	$TC_{ij} = \frac{1}{C_{ij}} \left( \frac{\Delta C_{ij}}{\Delta T} \right)_{\Delta T \rightarrow 0}, 10^{-5} K^{-1}$			-1.71	-0.96
$TC_{12}$				-4.65	-5.9
$TC_{44}$				-1.29	-1.5

Using the solutions of Green-Christoffel equations, earlier derived for explanation of small amplitude acoustic wave propagation in crystals, superposed with bias pressure [11], one can obtain

the relations between  $\alpha_v$  coefficients (1) and third-order elastic constants (Tab. 3). The procedure of the TOEC's calculation was executed by the Wolfram Mathematica 8 software including the least-square method option. Our results on the TOEC's complete set of diamond single crystal as well as known calculated and experimental data, are shown in the Tab. IV. Taking into account the results on second- and third-order elastic constants the theoretical calculation of the  $TC_{ij}$  coefficients by the relations [11] has been executed (Tab. 2).

As one can see from the Tab. 4, our results are close to the published earlier. The distinction between  $C_{456}$  constants can be explained by the relatively small effect concerned with such kind of constants, because in our experiments and calculations only the uniaxial pressure has been used. More essential effect would be expected if the shear stress was applied. The problem of more accurate definition of the  $C_{456}$  constant was known for other cubic crystals and hasn't solved for the present.

Table 3. Controlling coefficients for the some BAW modes of diamond

$N$	$U$	$P$	$\lambda_0 = \rho_0 v^2$	$\alpha_{v_i} = \frac{1}{v_i(0)} \left( \frac{\Delta v_i}{\Delta P} \right)_{\Delta P \rightarrow 0}$	$\alpha_{v_i},$ $10^{-13}$ $\text{Pa}^{-1}$
[001]	[001]	[110]	$C_{11}$	$\frac{1}{2\lambda_0} [2S_{12}C_{11} + S_{12}C_{111} + (S_{11} + S_{12})C_{112}]$	$-6.2 \pm 0.5$
	$[1\bar{1}0]$		$C_{44}$	$\frac{1}{4\lambda_0} [(2S_{11} + 2S_{12} - S_{44})C_{44} + (S_{11} + S_{12})C_{144} + (S_{11} + 3S_{12})C_{155} - S_{44}C_{456}]$	$-13.8 \pm 0.5$
	[110]		$C_{44}$	$\frac{1}{4\lambda_0} [(2S_{11} + 2S_{12} + S_{44})C_{44} + (S_{11} + S_{12})C_{144} + (S_{11} + 3S_{12})C_{155} + S_{44}C_{456}]$	$-15.6 \pm 0.5$
[110]	$[1\bar{1}0]$	[001]	$\frac{1}{2}(C_{11} - C_{12})$	$\frac{1}{4\lambda_0} [4S_{12}\lambda_0 + S_{12}C_{111} + (S_{11} - S_{12})C_{112} - S_{11}C_{123}]$	$-22.7 \pm 0.5$
	[110]		$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	$\frac{1}{2\lambda_0} [4S_{12}\lambda_0 + S_{12}C_{111} + (S_{11} + 3S_{12})C_{112} + 2S_{11}C_{144} + 4S_{12}C_{155} + S_{11}C_{123}]$	$-10.8 \pm 0.5$
	[001]		$C_{44}$	$\frac{1}{2\lambda_0} [2S_{11}C_{44} + S_{12}C_{144} + (S_{11} + S_{12})C_{155}]$	$-17.7 \pm 0.5$
	$[1\bar{1}0]$	$[1\bar{1}0]$	$\frac{1}{2}(C_{11} - C_{12})$	$\frac{1}{8\lambda_0} [2(2S_{11} + 2S_{12} + S_{44})\lambda_0 + (S_{11} + S_{12})C_{111} - (S_{11} - S_{12})C_{112} - 2S_{12}C_{123}]$	$-2.4 \pm 0.5$
	[110]		$\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$	$\frac{1}{8\lambda_0} [2(2S_{11} + 2S_{12} - S_{44})\lambda_0 + (S_{11} + S_{12})C_{111} + (3S_{11} + 5S_{12})C_{112} + 4(S_{11} + S_{12} - S_{44})C_{155} + 4S_{12}C_{144} + 2S_{12}C_{123}]$	$-10.9 \pm 0.5$
	[001]		$C_{44}$	$\frac{1}{4\lambda_0} [4S_{12}C_{44} + (S_{11} + S_{12})C_{144} + (S_{11} + 3S_{12})C_{155} - S_{44}C_{456}]$	$-14.2 \pm 0.5$

Table 4. Third order elastic constants  $C_{IJK}$  (GPa) of diamond at room temperature in comparison with previous data

	[5]	[6]	[7]	[8]	This work
$C_{111}$	$-6300 \pm 300$	-6475	-7367	$-7603 \pm 600$	$-7660 \pm 500$
$C_{112}$	$-800 \pm 100$	-1947	-2136	$-1909 \pm 554$	$-1550 \pm 500$
$C_{123}$	$0 \pm 400$	982	1040	$835 \pm 1447$	$3470 \pm 500$
$C_{144}$	$0 \pm 300$	115	186	$1438 \pm 853$	$-3130 \pm 300$
$C_{155}$	$-2600 \pm 100$	-2998	-3292	$-3938 \pm 375$	$-2630 \pm 300$
$C_{456}$	$-1300 \pm 100$	-135	76	$-2316 \pm 743$	$-700 \pm 300$

## Analysis of BAW Propagation in Diamond under the Uniaxial Stress Influence

Using the own software and data one obtained the anisotropy of BAW propagation parameters in the diamond under the uniaxial stress influence. As an example the results of anisotropic behavior of phase velocities and  $\alpha_v$  coefficients at different directions of pressure application for the waves, which can propagate along all the directions in the (001) crystallographic plane, are displayed on the Fig. 1.

When pressure is applied along [001] direction (Fig. 1b),  $\alpha_v$  coefficients for shear waves have the different values, and as a result the effect of removing of degeneracy for shear phase velocities has to be taken into account. Thus the acoustic axes along the [100] and [010] directions of undisturbed crystal should disappear. Actually, in this case the analysis of symmetry changing by Curie principle shows that the point symmetry of stressed crystal will be the tetragonal  $4mm$ , and the  $X$  or  $Y$  axis of such crystal will not have be the acoustic axis property. The insertion on the Fig. 1c shows that the acoustic axes, initially coinciding with [100] or [010] directions splits on two acoustic axis, inclined to the initial direction [11].

The greatest effect of the uniaxial pressure influence is observed for the longitudinal pressure application when pressure coincides with the wave normal (Fig. 1d) for all BAW types.

## Conclusion

For the first time the third-order elastic constants of synthetic diamond single crystal were obtained by direct ultrasonic measurement of BAW phase velocity variations under the action of uniaxial pressure. The results obtained are helpful for solid state physics in the field of analysis of anharmonic behavior of acoustic phonons, as well as for estimation of the diamond's prospective applications in the acoustoelectronic sensors of pressure or acceleration. Now there is the possibility of the systematic search for more effective crystalline directions and cuts to be used in such kind of devices.

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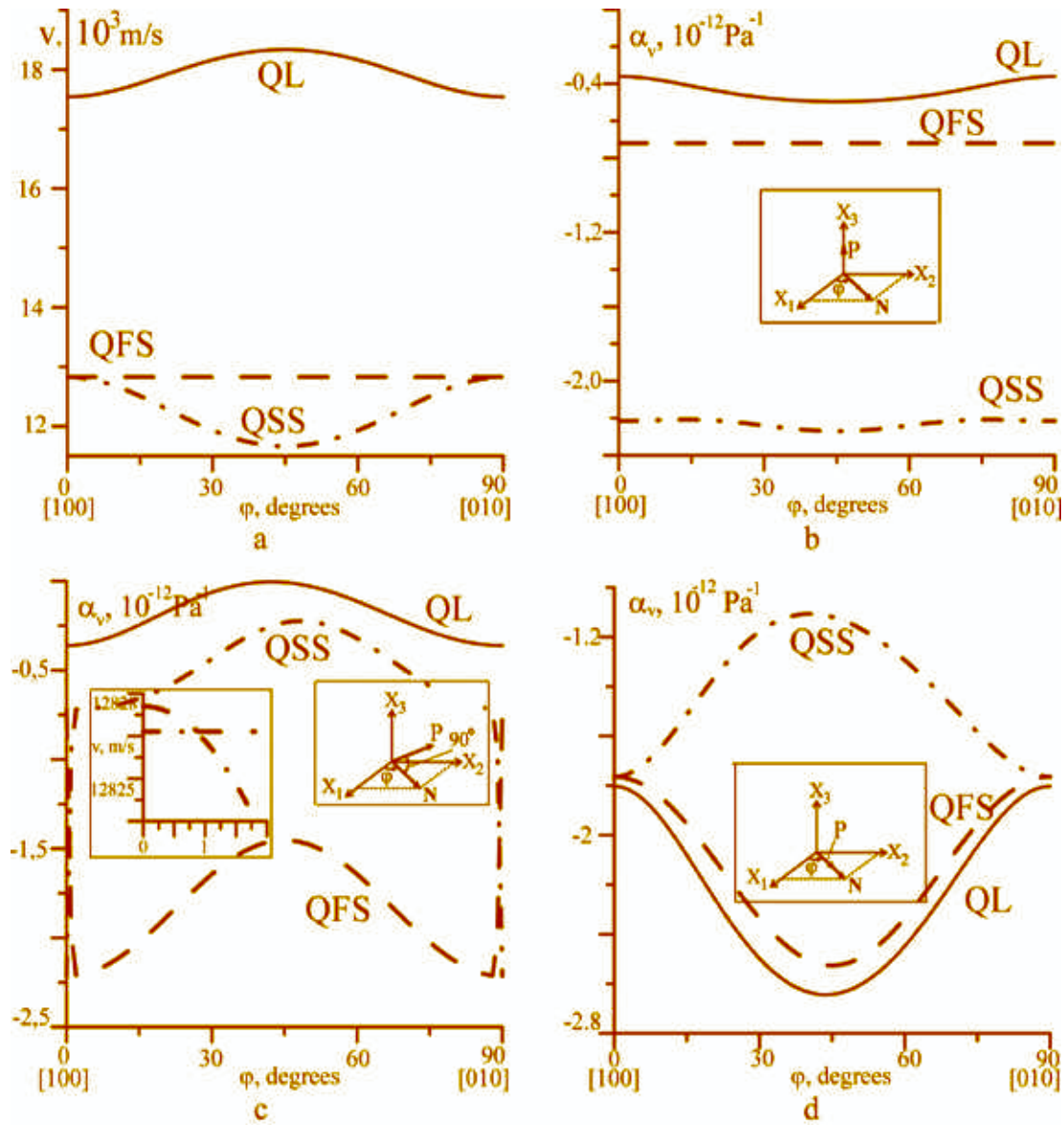


Fig. 1. Anisotropic behavior of phase velocities (a) and  $\alpha_v$  coefficients at the pressure application along [001] direction (b), perpendicularly to the wave normal (c), and along the wave normal (d) for the waves, which can propagate along all the directions in the (001) crystallographic plane.

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## Экспериментальное исследование линейных и нелинейных упругих свойств синтетического монокристалла алмаза

Борис П. Сорокин  
Геннадий М. Квашнин  
Михаил С. Кузнецов  
Арсений В. Теличко  
Сергей И. Бурков

Представлены экспериментальные результаты по исследованию распространения объемных акустических волн (10–200 МГц) в синтетических монокристаллах алмаза под воздействием одноосного давления и температуры. Полученные данные по упругим постоянным второго и третьего порядка были использованы для расчета характеристик анизотропии распространения акустических волн в алмазе под давлением. Обсуждаются особенности распространения волн.

Ключевые слова: объемная акустическая волна, одноосное давление, влияние температуры, синтетический алмаз, упругие постоянные второго и третьего порядка.