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COMBUSTION, EXPLOSION,  
AND SHOCK WAVES

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## Structural Nonuniformity of Detonation-Produced Diamond-Containing Material

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**Abstract**—Raman backscattering spectra (RBS), infrared spectra, and X-ray diffraction intensity curves for various fractions of ultradispersed diamond-containing material (UDDCM) were recorded. The RBS and XRD curves obtained suggest that UDDCM is characterized by sharp variations in the ratio between the diamond and nondiamond components, a factor that makes it possible to consider this phase as an individual product and determines the scale of variations in the main characteristics. Fine UDDCM fractions contain only small amounts diamond-like ( $sp^3$  carbon) grains, if any. One possible reason for changes in the ratio between the phases is density fluctuations under nonequilibrium conditions of synthesis.

**Keywords:** diamond-like material, structural nonuniformity, Raman scattering spectroscopy.

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### INTRODUCTION

In the present work, we studied detonation-produced ultradispersed diamond-containing material (UDDCM) [1, 2]. This structurally nonuniform material consists of nondiamond carbon, molecular fragments, functional groups, and diamond-type ( $sp^3$ ) carbon. The properties of fine UDDCM fractions obtained by centrifugation and mechanical destruction differ significantly. For example, according to [3], the carbon content in fine UDDCM particles is low, 84%. This suggests that the distribution of diamond and nondiamond fractions in fine UDDCM particles, i.e., light fractions, may be variable. The aim of the present work was to study the distribution of  $sp^3$  carbon in fine UDDCM fractions.

### EXPERIMENTAL

Raman backscattering spectra (RBS) were recorded on a Bruker RFS100/S Fourier spectrometer over a frequency range of 100 to 4000  $\text{cm}^{-1}$  at a resolution of 1  $\text{cm}^{-1}$ . The excitation source was a Coherent Compass 1064-1500N Nd : YAG laser with diode pumping (1.6  $\mu\text{m}$ , 800 mW). To record spectra within 1200–1800  $\text{cm}^{-1}$ , we used a Jobin Yvon T64000 spectrometer. Excitation was accomplished with an Ar<sup>+</sup> laser ( $\lambda = 514.5$  nm; irradiance power at the sample, 37 mW). Measurements were conducted with the help of a microscope. The IR absorption spectra were recorded on a Specord M-82 instrument with computer processing and a Vertex-44 Fourier spectropho-

tometer. The spectra were recorded within a spectral range of 400 to 4000  $\text{cm}^{-1}$ . The samples were mixed with potassium bromide and pressed into pellets. RDX diffraction intensity curves were recorded on an XRD-6000 Shimadzu diffractometer. The UDDCM samples were synthesized in a mixture of high explosives in an atmosphere of carbon dioxide (UDDCM-1) or nitrogen (UDDCM-2). UDDCM-1 was synthesized by detonating a TNT/RDX mixture, whereas UDDCM-2 was obtained by detonating TNT/RDX, trinitroresorcin/RDX, and trinitrobenzene/RDX mixtures. The UDDCM-1 sample was extracted from the detonation products by oxidation in the presence of boron anhydride; the UDDCM-2 was extracted by using treatment with perchloric acid. An analysis of the IR and RB spectra of initial UDDCM spectra was conducted in [4, 5], where the effect of the molecular component on the pattern of these spectra was considered.

Fractionation was performed on a TsLN-2 centrifuge operating at 9000 rpm. The hydrosols obtained contained 10–50 g/l UDDCM. The duration of centrifugation was 5 min. The mass of the light fraction of UDDCM-1 after centrifugation at 3000 and 5000 rpm was 2.1% of the mass of the initial material. The IR spectra of the light and heavy fractions of UDDCM-1 showed no appreciable qualitative distinctions. The IR and RB spectra of UDDCM-2 samples are displayed in Figs. 1 and 2. The molecular groups identified in [4, 5] were present in both the light and heavy fractions of UDDCM-1 and UDDCM-2. In the light fraction of

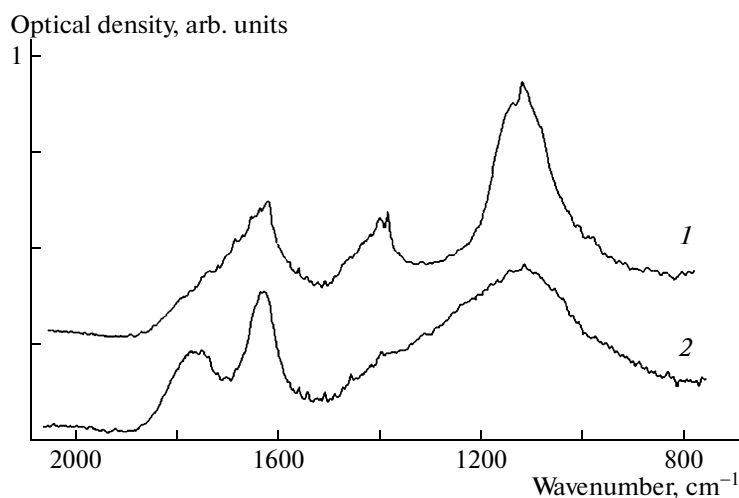


Fig. 1. Infrared absorption spectra of (1) light and (2) heavy fractions of UDDCM-2.

UDDCM-2, the concentration of carboxyl and carbonyl groups was found to be lower. XRD measurements showed that the content of the diamond phase ( $sp^3$ ) in the light fraction is substantially smaller. In the RBS of the light fraction, the intensity of the diamond phase band (at  $1333\text{ cm}^{-1}$ ) was markedly lower: in Fig. 4, this band is absent, which confirms this result (Figs. 1–4). UDDCM appears to be a separate dense phase, which is characterized by a variable content of the diamond ( $sp^3$  carbon) and nondiamond ( $sp^2$  carbon, molecular fragments, functional groups) components. This variability in the content of the diamond and nondiamond component makes this product individual and determines the scatter in the main characteristics, as discussed in [4]. Because of a relatively

high density, the chemical stability of this phase is rather high.

## DISCUSSION

A sharp change in the ratio between the diamond and nondiamond components of UDDCM observed in experiment means that the particles of this material exhibit a density gradient, which suggests that such a material is likely to be formed under the nonequilibrium conditions of the detonation wave, with sharp changes of the pressure or density. In our previous work [4], we assumed that density fluctuations affect the synthesis for the following reasons:

(1) Experiments showed that the HE density influences the UDDCM yield and that the temperature of synthesis affects the UDDCM grain size [6, 7], more specifically, the UDDCM yield increases with the density of the initial HE and, hence, the density of material under explosion conditions. The fundamental limitation is the impossibility to obtain denser HEs [1, 6, 7]. In the first approximation, the efficiency of the synthesis can be described by the relationship  $F = (a\rho^b kT)/V$ , where  $a$  and  $b$  are coefficients,  $\rho$  is the density of the material in the synthesis zone,  $T$  is the synthesis temperature,  $k$  is the Boltzmann constant,  $V$  is the volume of a primary UDDCM particle. This function is believed to contain information on the character of density fluctuations.

(2) That fluctuations influence the process of synthesis was showed in a theoretical work [10].

(3) In [8, 9], small-angle X-ray scattering (SAXS) analysis of the detonation products was performed with the aim to study density gradients. Previously, it was believed that such gradients exist only between diamond grains and the ambient material. The experiment performed in the present work demonstrated

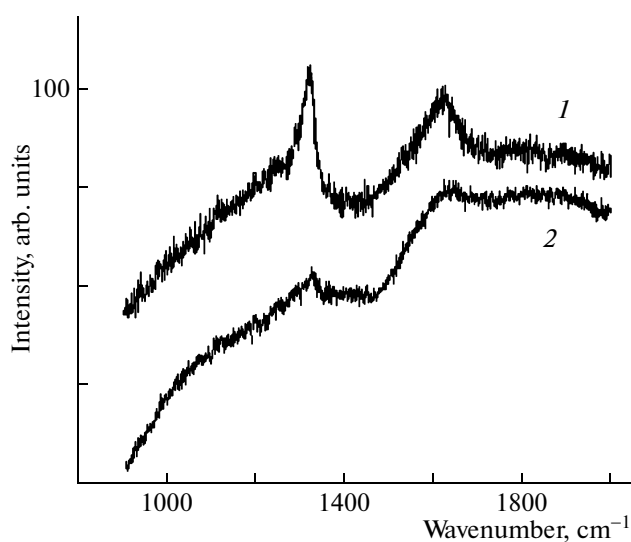
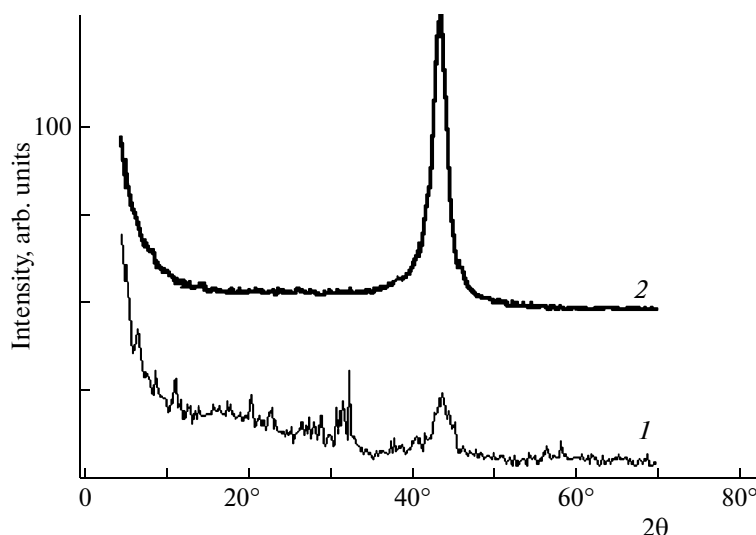
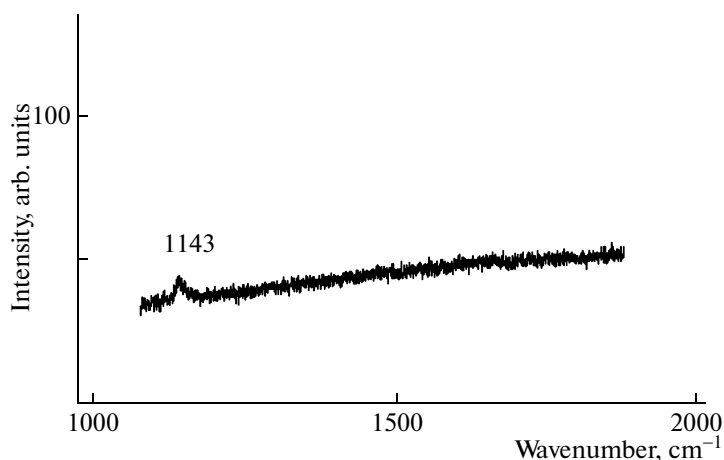


Fig. 2. Raman backscattering spectrum of (1) the initial sample and (2) light fraction extracted from it by centrifuging at 3000 rpm.



**Fig. 3.** Diffractograms of the (1) light and (2) heavy fractions of UDDCM-2 (extracted at 3000 rpm). For the light fractions, the scattering intensity within  $2\theta = 10^\circ\text{--}20^\circ$  is higher than the intensity of the main peak belonging to the diamond phase, which is indicative of a low concentration of the diamond phase.



**Fig. 4.** Raman backscattering spectrum of the light fraction of UDDCM-1 extracted by centrifuging at 7000 rpm. No traces of the diamond phase are detectable.

that some of the light fractions contain no diamond grains at all.

The results of SAXS measurements can be interpreted as an interplay of three main factors. First, the growth of individual particles gives rise to density gradients and, as a result, an increase in the SAXS signal. Second, an increase in the number of UDDCM particles also causes an increase in the signal. Third, the SAXS signal increases due to dynamic density gradients. Such dynamic regions of compression and rarefaction can arise in the material itself due to a nonlinear wave process capable of creating spatial variations in the density. Interacting with the ambient medium, some of such centers give rise to UDDCM particles, whereas the others disappear. The formation of condensed UDDCM particles can be treated in terms of

the interaction of this wave process with the ambient medium.

Experiments on studying the effect of the shell and its thickness on the intensity of the SAXS signal suggest [8, 9] that the shell, giving rise to secondary reactions, retards the formation of UDDCM. The main parameters that affect the preservation of UDDCM are the volume of the explosion chamber, the buffer gas pressure, and density of the HE charge. These observations can be interpreted by assuming that the SAXS signal stems from a chemically active volume or a process creating a dynamic density gradient. The interaction of this process with the ambient medium, i.e., the condensation of material as an equilibrium process is controlled by secondary processes, which, in turn, are influenced by the explosion chamber volume

or the shell thickness. It was demonstrated [8, 9] that the intensity of the SAXS signal depends on whether the HE used is aromatic or not, a result implying that chemical reactions influence the characteristics of the density gradients formed. The effect of the chemical reactions, in turn, depends on the initial state and density of the HE charge.

Another aspect discussed in [8, 9] concerns the effect UDDCM additives to the HE charge. The experimental results obtained suggest that the signal source is a chemically active object. Therefore, when an inert (nonexplosive) material (UDDCM) is added to the HE, the SAXS signal decreases; i.e., an inert additive suppresses active physicochemical processes, thereby retarding the formation of regions of dynamic compression and rarefaction regions.

We believe that, in the third case, the source of dynamic density gradient in nonequilibrium detonation processes can be density fluctuations. Note also that the nonlinear density distribution in the reaction zone suggests that fluctuations directly influence the process of energy release.

### CONCLUSIONS

Thus, in the present work, Raman backscattering spectra and infrared spectra of various fractions of ultradispersed diamond-containing material were recorded. The RBS and XRD curves obtained suggest that UDDCM is characterized by sharp variations in the ratio between the diamond and nondiamond components, a circumstance that allows one to consider

this phase as an individual product and determines the scale of variations in the main characteristics. Fine UDDCM fractions contain only small amounts diamond-like ( $sp^3$  carbon) grains, if at all. Changes in the SAXS signal that arise due to dynamic density gradients may be associated with the direct influence of density fluctuations, the intensity of which should be significant under nonequilibrium conditions in the detonation wave.

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