# New nanocluster carbyne-based material synthesized under high pressure

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DC and AC conductivities, magnetoresistance and thermopower of carbyne samples were studied over the temperature range 1.8–300 K at frequencies 10 MHz–1 GHz. It was established that a variation in the fraction of $sp^2$ bonds in carbynes induces transition from one- to two- and then to three-dimensional conduction. The physical properties of the new carbyne-based solids may be understood within the model treating carbyne as a nanocluster material based on linear carbon chains and having characteristic cluster size 1-10 nm.

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**1**. Carbyne is an allotropic carbon form based on *sp*-type bonds and possessing a pronounced linear-chain structure [1–3]. Contrary to other allotropic modifications with $sp^2$ (graphite) or $sp^3$ (diamond) bonds, carbyne cannot be synthesized as a perfect crystal, because its chains contain "built-in" disorder, probably due to the instability of large linear carbon clusters [3]. Although up to now there is no commonly accepted model structure of carbyne, it is customarily believed that linear *sp* segments of the polymeric carbon molecule in carbyne alternate with $sp^2$-hybridized carbon atoms [1–3]. The $sp^2$-centers give rise to chain kinks, and the dangling bonds appearing at the kinks may attach impurity atoms or form interchain links (in the absence of the $sp^2$-defects, the carbon chains are bonded by weak van der Waals forces). As a result, the carbon chains may form complex globular structures.

The fraction of $sp^2$-bonds in carbyne can be varied smoothli by applying high pressure and temperature [1]. An increase in the synthesis temperature $T_{\text{syn}}$ under pressure induces the $sp \to sp^2$ transition, i.e., the formation of a disordered 2*D* graphite-like network from the structure dominated by 1*D* chains. Therefore a carbynes synthesized under high pressure open an intriguing opportunity of creation of experimental system with variable dimensionality [4]. In the present work we report results of the study of DC and AC conductivity, magnetoresistance and thermopower measured in the temperature, frequency and magnetic field domain $1.8 < T < 300$ K, 1 MHz $< \nu <$ 1 GHz and $B < 7$ T.

**2**. Carbyne with chains $\ldots{=}C{=}C{=}C{=}C{=}\ldots$ of the cumulene type was synthesized at the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, and used as starting material. Samples were prepared by the method used in [1]. Synthesis was carried out at a pressure of 7.7 GPa. At different $T_{\text{syn}}$ values the sample structure was identical to that described in [1]. The temperature dependences $\rho(T)$ for different $T_{\text{syn}}$ temperatures are shown in Fig. 1, *a*. In coordinates $\log(\rho) = f(T^{-\alpha})$ linear segments characteristic to variable range hopping (VRH) conductivity are clearly seen in the curves at $T < T^* \sim 40$ K down to $T \sim 1.8$ K. The index $\alpha$ which, for the constant density of states and space dimension $d$, is given by [5]

$$\alpha = 1/(d+1), \qquad (1)$$

increases with decreasing synthesis temperature (Fig. 1). A value of 1/4 found for this parameter for $T_{\text{syn}} = 890°$C corresponds to the 3*D* Mott's law, while the reduction in $T_{\text{syn}}$ to 800°C increases $\alpha$ to 1/3, which is characteristic of 2*D* hopping conduction (Eq.(1)). In the vicinity of $T_{\text{syn}} \sim 700°$C, the exponent changes to 1/2 (Fig. 1, $T_{\text{syn}} = 690°$C) that suggests transition to 1*D* hopping transport.

Thus, one can assume that the rise in the temperature of synthesis under pressure induces crossover from 1*D* to 3*D* hopping conduction. In the transition region $700 < T_{\text{syn}} < 800°$C, the carbyne matrix represents a set of mutually noninteracting 2*D* carbon layers. Such an interpretation qualitatively agrees with the data [1] on the $sp \to sp^2$ transition, because the "degree of cross-linking" between the carbon chains increases with $T_{\text{syn}}$ and the effective dimensionality of the system should increase. Note that, according to [1], carbyne samples undergo "graphitization" at $T_{\text{syn}} \sim 700°$C, so that the crossover first to 2*D* and than to 3*D* conduction at $T_{\text{syn}} > 700°$C seems to be quite natural.

At the same time, it was assumed in [1] that a quasi-one-dimensional structure occurs in carbyne at $T_{\text{syn}} < 500°$C, while in the samples obtained at higher temperatures the fraction of $sp^2$-bonds is appreciable. Because of this, the interpretation of the data in Fig. 1 as a $1D \to 2D \to 3D$ transition is not unique. For example, the $\alpha = 1/2$ value may be explained by the appearance of a Coulomb gap in a 2*D* hopping sustem [4,5].

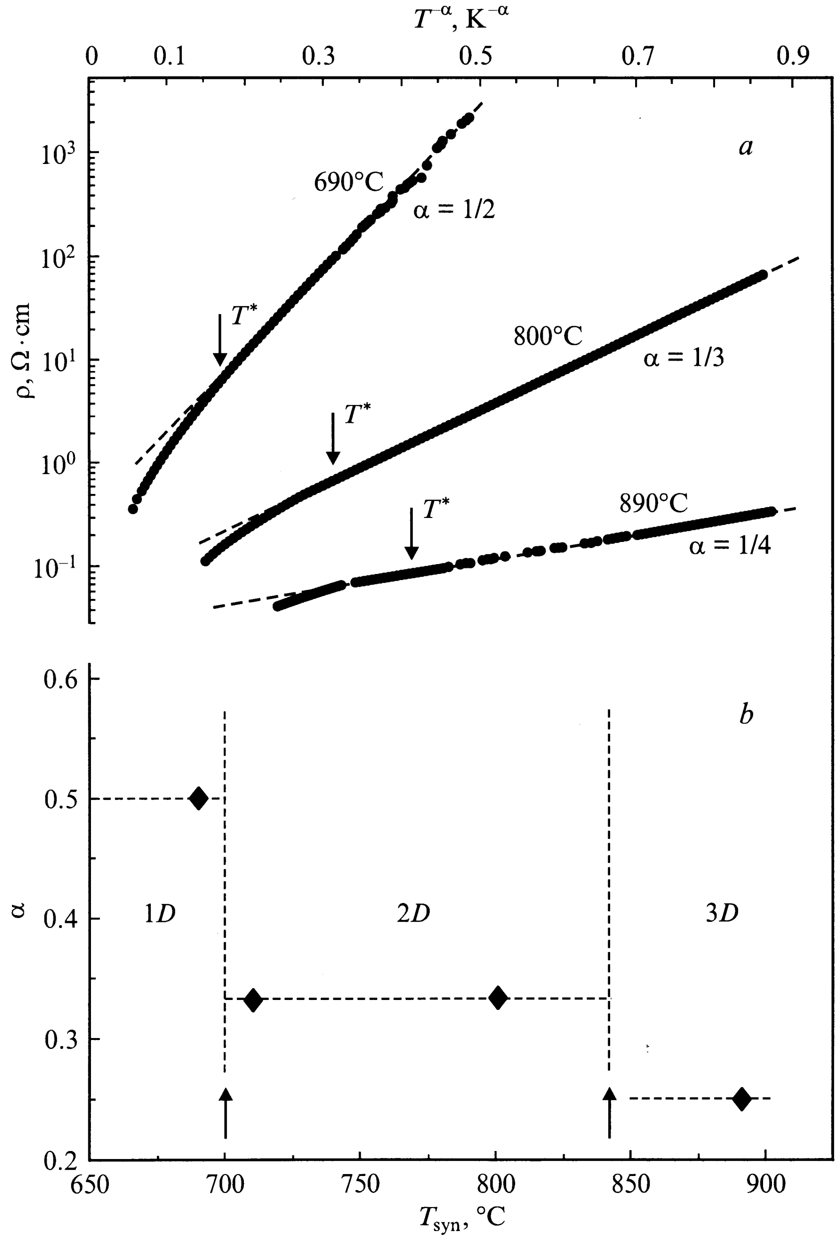

**Figure 1.** Temperature dependence of conductivity (*a*) and hopping conduction exponent (*b*) for carbyne samples synthesized at different temperatures.

The latter possibility is eliminated by analysis of AC conductivity data. In 2*D* or 3*D* case with Coulomb correlations the hopping conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ at frequency $\omega$ is given by [4,6]

$$\sigma_1, \sigma_2 \sim \omega^s T^\alpha \qquad (2)$$

with the practically temperature-independent index $s$. Contrary to this expectation, experiment shows strong $s(T)$ dependence (Fig. 2) which is characteristic for the 1*D* systems. Indeed, according to the Hunt's calculation for a 1*D* system [7,8]

$$s(T) = \left[(AT_0/T)^{1/2} - 2\right] / \left[(AT_0/T)^{1/2} + 2\right], \qquad (3)$$

where $T_0$ is the same as in the temperature dependence of DC conductivity $\ln\sigma \sim -(T_0/T)^\alpha$ while parameter $A$ depends on the length of linear hopping chain $L$ and localization radius $a$: $A \approx \exp(2)L/a$. Comparison of Eq. (3) with the experiment shows that Hunt's theory describes well observed $s(T)$ data assuming reasonable value $L/a \sim 680$ (curve *4* in Fig. 2).

An additional argument against opening of the Coulomb gap in carbynes obtained at $T_{syn} < 700$°C is provided by thermopower measurements. In the VRH regime at $T < T^*$ thermopower is proportional to first derivative of the density of states (DOS) [6]. Therefore for the Coulomb gap regime where DOS is symmetric with respect to the Fermi level, the

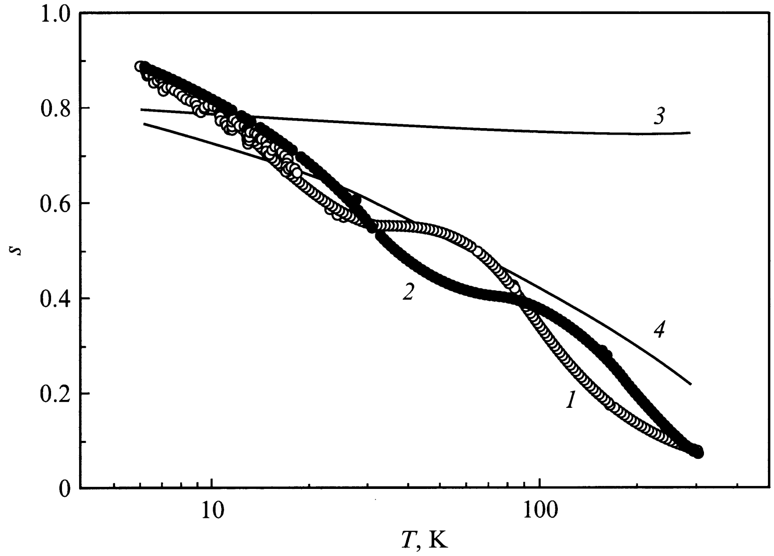

**Figure 2.** Temperature-dependent exponent $s$: experiment with 100 MHz (*1*), experiment with 500 MHz (*2*), model of Coulomb correlations for $d = 2$ (*3*), and Hunt's model for $d = 1$ (*4*).

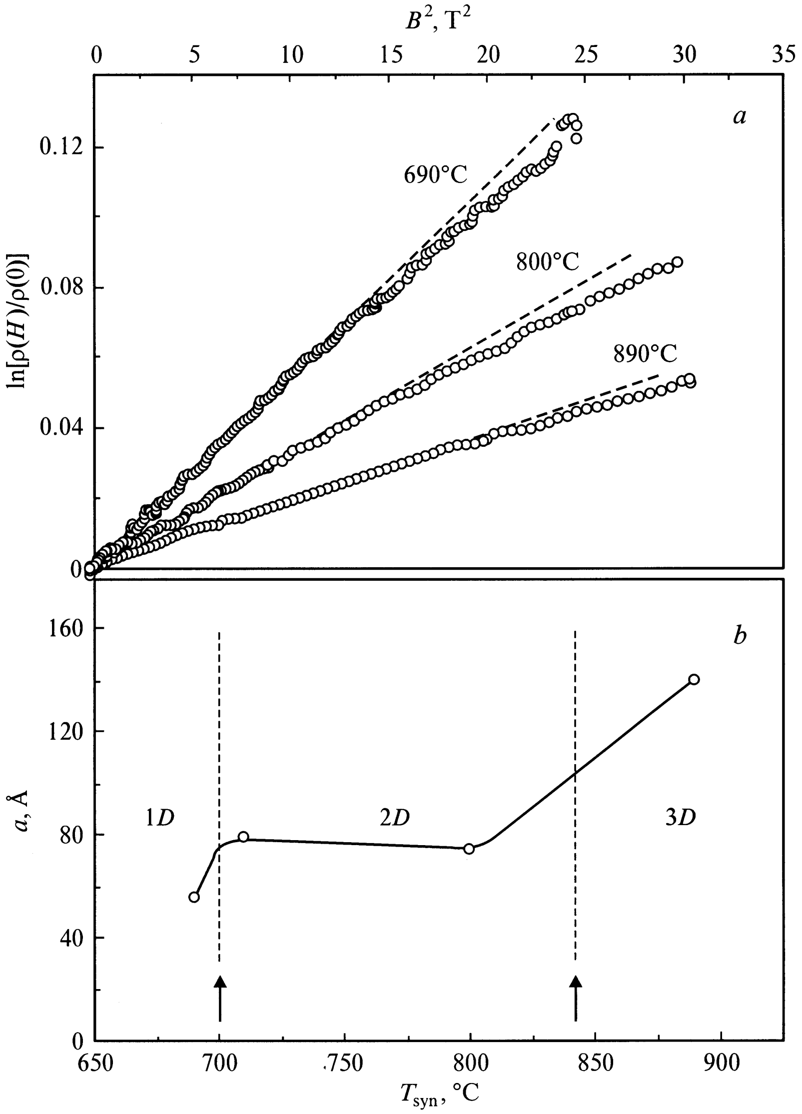

**Figure 3.** Magnetoresistance (*a*) and localization radius (*b*) for carbyne samples synthesized at difference temperatures.

Seebeck coefficient should be equal to zero. At the same time we find that for all the samples studied, including those with $\alpha = 1/2$, the thermopower remain finite in the hopping region. The observed behaviour is consistent with the above explanation of the values $\alpha > 1/4$ by $1D \to 3D$ crossover and disagrees with the opening of the correlation gap at the Fermi level.

**3**. Study of the VRH regime opens an opportunity to determine the localization radius. The shrinkage of the wave function in magnetic field gives rise to the positive magnetoresistance

$$\ln[\rho(B)/\rho(0)] = t_d a^4 B^2 (T_0/T)^{3\alpha}/c^2\hbar^2, \qquad (4)$$

where coefficient $t_d$ depends on the space dimension: in $2D$ $t_2 = 1/360$ [9] and in $3D$ $t_3 = 5/2016$ [10]. Experimental $\rho(B)$ data at $T = 4.2\,\mathrm{K}$ are shown in Fig. 3, *a*; it is visible that Eq. (4) provides a good approximation of magnetoresistance in carbynes synthesized at different $T_{\mathrm{syn}}$. Taking slopes of linear parts in coordinates $\ln\rho = f(B^2)$ together with the $T_0$ values calculated from Fig. 1, *a* we found localisation radius values for $T_{\mathrm{syn}} > 700°\mathrm{C}$ (see Fig. 3, *b*, regions $2D$ and $3D$). In $1D$ case (i. e. at $T_{\mathrm{syn}} < 700°\mathrm{C}$) the exact value of $t_d$ is unknown, therefore we used $t_2$ to get an estimate (Fig. 3, *b*).

The obtained $a(T_{\mathrm{syn}})$ data demonstrate a clear increase of localization radius with synthesis temperature. In $1D$ case we find $a \sim 60\,\text{Å}$, whereas for $2D$ case the localization radius reaches $\sim 80\,\text{Å}$. The region of $3D$ VRH ($T_{\mathrm{syn}} > 840°\mathrm{C}$) is described by $a \sim 140\,\text{Å}$, that is 2.3 times higher than in $1D$ (Fig. 3, *b*). It is worth to compare obtained data on localization radius with the structural characteristics of the disordered carbyne matrix. $X$-ray structural analysis gives medium range order length $L_{\mathrm{MRO}} \sim 8-10\,\text{Å}$ for initial carbyne powder, and for the samples studied in the present work $L_{\mathrm{MRO}}$ is about 10–12 Å. These values are of the same order of magnitude as expected for the maximal stable linear cumulene fragments in carbyne structure [2,3] but $5-14$ times lower than observed values of localization radius. Therefore the localization in disordered potential of carbyne matrix have a multicenter nature.

On the other hand, in a strongly disordered solid like carbyne the spatial scale $a \gg L_{\mathrm{MRO}}$ may be relevant to some structural elements of disordered network [11], for instance may correspond to a clusters or physical inhomogeneties with higher conductivity having size $\sim a$ and formed from linear fragments having size $\sim L_{\mathrm{MRO}}$. The check of this hypothesis requires further structural study of carbynes synthesized under high pressure.

The obtained results allow one to refine the scenario of the $sp \to sp^2$ transition [1]. Since the $1D$ conduction persists up to $T_{\mathrm{syn}} \sim 700°\mathrm{C}$, the appearance of new $sp^2$-centers likely leads to the disorder and bending of individual chains in this range of synthesis temperatures. At $T_{\mathrm{syn}} > 700°\mathrm{C}$, the increase in the fraction of the $sp^2$-bonds induces cross-linking between the chains, rendering the conduction two-dimensional. At further increase of $T_{\mathrm{syn}}$ giving rise in the concentration of $sp^2$-centers in the carbyne matrix, the topology of quasi-two-dimensional carbon layers becomes more complicated and they start to interact with each other, leading to the $3D$ character of conduction.

The obtained values of localisation radius and $X$-ray structural data suggests that carbyne matrix can be likely treated as a nanocluster material having characteristic cluster size 1–10 nm and based on linear fragments of carbon chains. A complicated spatial hierarchy of disordered carbyne matrix together with an intriguing possibility of the variation of the effective dimension of space where charge carriers moves from $1D$ to $3D$ via $2D$ makes prospective future fundamental and applied studies of these solids.

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