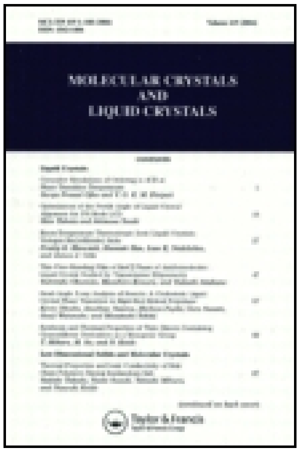

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

High Pressure for Synthesis and Study of Superdense Alkali Metal - Carbon Compounds

Vera A. Nalimova [a]

[a] Department of Chemistry and Physics of High Pressures, Moscow State University, Moscow, 119899, Russia

To cite this article: Vera A. Nalimova (1998): High Pressure for Synthesis and Study of Superdense Alkali Metal - Carbon Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 5-18

To link to this article: http://dx.doi.org/10.1080/10587259808045308

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 5–17
Reprints available directly from the publisher
Photocopying permitted by license only

High pressure for synthesis and study of superdense alkali metal - carbon compounds

VERA A. NALIMOVA
Department of Chemistry and Physics of High Pressures, Moscow State
University, Moscow, 119899, Russia

Intercalation of alkali metals into graphite and other carbon matrices with large volume decrement is favored by high pressures: the temperature of the reaction decreases and the amount of intercalated metal increases 2 to 3 times in comparison with the compounds obtained under traditional conditions. Superdense alkali metal in carbon matrices exposes unusual valence state with high degree of p- and d-states in chemical bonding.

Keywords: High pressure, alkali metals, graphite, fullerenc, carbon nanotubes

INTRODUCTION

According to the Le Chatelier principle the effect of high pressure is the most pronounced if the reaction is accompanied by the substantial volume decrease. Alkali metal intercalation into aromatic carbon matrices such as graphite, fullerene, carbon nanotubes meets this condition (Table 1). The other reason of the great promise of high pressure application for these reactions lays in the nature of alkali metals. Chemical reactivity of alkali metals can be profoundly altered under pressure because large changes can be induced in their electronic configuration, chemical bonding, and atomic size. Under pressure the outermost *s*-electrons of alkali metal collapse to *d*-like states giving the electronic configuration (d^1) of a transition element [1]. S-to-d transfer starts at pressures close to ambient and proceeds gradually thus affecting the alkali metal properties even at moderate pressures. Although considerable attention has been focused on the changes in physical properties of the alkali metals under pressure, the effect of the s-to-d transition on the formation of chemical compounds has hardly been explored experimentally. The recent results on Ni-K interactions [2] at pressures above 300 kbar, where the d-character of K is greatly enhanced demonstrate that the chemical behavior of alkali metals under pressure is very different from that under ambient conditions. The availability of the d-electron bonding states of alkali metals should also allow new chemistry with many of the nonmetallic elements. The investigation of high pressure interaction of alkali metals with aromatic carbon matrices offers new exciting possibility to study pressure-induced alkali metal chemistry and moreover to stabilize the transition metal-like state (d^1) of alkali metal at ambient conditions.

TABLE 1 Volume effects of alkali metals intercalation into different carbon matrices

Graphite compounds	-ΔV,%	C_{60} and nanotubes compounds	-ΔV, %
LiC_6	21.6*	K_3C_{60}**	23.0
KC_8	23.2*	Rb_3C_{60}**	24.2
RbC_8	26.6*	K_6C_{60}**	27.2
CsC_8	32.9*	Cs_6C_{60}**	20.6
LiC_2	50.3*	$Li_{12\text{-}20}C_{60}$*	26.4-43.6
KC_4	40.1*	$Na_{9\text{-}16}C_{60}$*	29.8-47.0
RbC_4	44.9*	$(Na_2K)_{4.7}C_{60}$	20.1
CsC_4	48.2*	$LiC_{0.8\text{-}1}$ (C=MW nanotubes)*	28.0

* - experimental; ** - calculated from XRD data

HIGH PRESSURE ALKALI METAL - CARBON SYNTHESIS

Alkali metals in liquid, gas phase and solution easily intercalate graphite forming LiC_6 and MC_8 (M = K, Rb, Cs) compounds as the richest with alkali metal. For the first time the effect of high pressure on alkali metal density in graphite galleries was shown by S. Solin et al. [3] in their investigations of staging transitions in stage 2 K-GICs: $KC_{12x2} \rightarrow KC_{8x3}$. The staging transitions were accompanied by alkali metal density increase in the layers but maximum metal contents was still MC_8. Later J.E. Fischer et al. [4] were the first to show the possibility of having MC_6 layer (for heavy alkali metals) as a result of staging transitions in KC_8 under pressure: $6KC_{8x1} \rightarrow 4KC_{6x1} + K_2C_{8x3}$ (at 15 kbar) and $K_2C_{8x3} \rightarrow 2KC_{6x2}$ (at 19 kbar). Both high pressure investigations were carried out on the compounds synthesized by traditional ways.

The first direct high pressure synthesis of alkali metal GICs was carried out by D. Guerard et al. [5], however the synthesis yielded "normal" LiC_6 compound. The idea of obtaining the compounds with higher alkali metal contents (than LiC_6 and MC_8) under pressure was based on the large volume decrement at alkali metal intercalation into graphite (Table 1). The investigations on the high pressure synthesis started in Moscow State University at the Department of Chemistry and Physics of High Pressures in early 1980-s [6]. Actually the high pressure intercalation of alkali metals into graphite yielded the compounds with extraordinary high metal contents: MC_{2-3} (M = Li, Na) and MC_4 (M = K, Rb, Cs) (Table 2).

The same effect of the high pressure was expected in case of alkali metal intercalation into (interaction with) different carbon - based materials. The intercalation of alkali metal into aromatic carbon matrices other than graphite (such as fullerene, carbon nanotubes) is also accompanied by the considerable volume decrease (Table 1) indicating that high pressure is rather promising for synthesis of new compounds with high metal density.

High pressure synthesis [18,19] yielded already the fullerene and carbon

TABLE 2 High pressure synthesis and properties of alkali metal - carbon compounds

Com pound	Conditions	T$_c$, K	Stability
LiC_2	>8 kbar, 300^0, DTA [6]; 40-80 kbar, 280^0, volumetry [7]	2.1 [8]	decompose slowly to ~$LiC_{3.4}$ [9]
KC_4	>5 kbar, 150^0, DTA [6]; 6-10 kbar, 160-170^0, volumetry [10]; 20-40 kbar, 20^0, optical reflection [12]	~5 [11]	decompose rapidly to KC_8 below 1.5 kbar [10]
$RbC_{4.5}$	20-25 kbar, 20^0, volumetry [13]	1.6	decompose to $RbC_{6.5}$ below 2 kbar
CsC_4	2 kbar, 20^0, volumetry [10]	~6 [10]	(meta)stable
$NaC_{2\text{-}3}$	35-45 kbar, 450^0, XRD at 100 K [14]; 40 kbar, 350^0, volumetry, DTA [15]	2-5 [14]	decompose at P < 20 kbar [14,15]
NaC_4	>30 kbar, 900^0, DTA [16]	-	stable (due to O^{2-}?)
$KRb_{1.1}C_8$	3-10 kbar, 20^0, volumetry [17]	1.5	(meta)stable
$KCs_{1.2}C_8$	2-6 kbar, 20^0, --"--	1.2	--"--
$KNa_{1.3}C_8$	60 kbar, 200^0, --"--	1.6	--"--
$Na_{10\text{-}16}C_{60}$	50 kbar, 400^0, volumetry, DTA [18]		--"--
$Li_{12\text{-}20}C_{60}$	55 kbar, 280^0, --"--		--"--
LiC_1 nanotubes	45 kbar, 280-300^0, volumetry, XRD [19]		--"--

nanotubes compounds with high alkali metal contents: such as $Li_{12\text{-}20}C_{60}$, $Na_{16}C_{60}$, LiC (C = carbon nanotubes) stable under ambient conditions (Table 2). It should be noted that these carbon matrices offer even more rich possibilities for the high pressure synthesis than graphite. Graphite preserves its structure under pressure (at synthesis conditions) whereas the structure of pristine C_{60} is strongly affected by high pressures [20]. According to ourresistivity *vs* P, T data

C_{60} undergoes at least two phase transitions under synthesis conditions [21] and intercalation proceeds into a modified fullerene structure. IR spectroscopy of Na- and Li-C_{60} compounds shows that these modifications are preserved in the intercalation compound at ambient pressure. So varying synthesis conditions one can obtain the compounds of alkali metal and C_{60} in different modifications. As concerning carbon nanotubes the resistivity and volume *vs* pressure measurements, XRD and IR-spectroscopy did not reveal any irreversible or reversible 1 order phase transitions under synthesis conditions neither for multiwall nor for singlewall nanotubes in the limits 90 kbar, 400^0 C.

High pressure techniques

The high pressure synthesis techniques here described were elaborated basically for alkali metal GICs and afterwards used for carbon materials other than graphite. They enable to work under pressure upto 90 kbar and temperature to 1500^0C. Despite of the high pressure technique breakthrough initiated by the research in diamond synthesis, high pressure is mostly used for the investigations of physical properties of elements and compounds and strictly technological purposes rather than for studying of chemical reactions.

The main advantage of devices used is the opportunity to provide *in situ* control of the reaction under pressure. It may be achieved in two ways: by differential thermal analysis introducing two thermocouples into a high pressure cell [22,6]; or by the volumetric technique which enables to determine the volume of the sample under pressure with accuracy 0.07-0.20% [10]. Both techniques enable to control a reaction under pressure *in situ* and to identify the first-order phase transitions *vs* pressure. The volumetric technique also provides the information on the density, compression and volume compressibility of the compounds obtained.

For the high pressure synthesis we mostly use the following devices:

- Anvil apparatus with either lenticular (Fig.1) or toroid high pressure cell and with internal heating of the cell by the resistance graphite furnace which provides the possibility to carry out synthesis at temperatures upto 1500°C, pressure limit 90 kbar. The cells made of pyrophyllite are shaped to fit in the profile of tungsten carbide anvils and designed to permit the differential thermal analysis T(ΔT) (either T(time)) *in situ* [22]. Modification of the assemblies makes possible resistivity *vs* pressure (and *vs* temperature at given pressure) measurements both in lenticular and toroid cells.. Using a toroid cell we gain in pressure but loose in volume of the sample compare to a lenticular cell. The pressure in the cell is calibrated by the measurement of electrical resistance of a bismuth wire *vs* pressure at known transition points BiI-BiII, BiII-BiIII, BiV-BiVI.

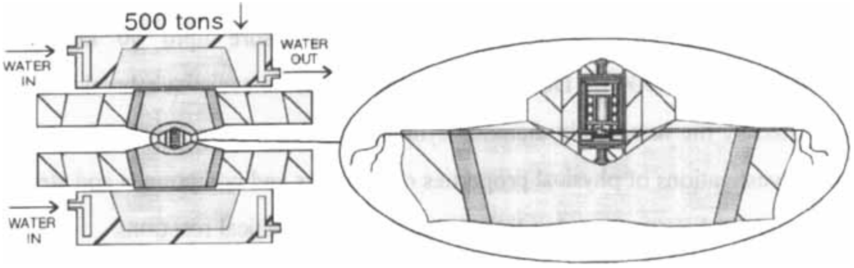

FIGURE 1 Anvil - lenticular cell high pressure device with internal heating of the cell and DTA control of the reaction

- The high pressure piezometer with piston - cylinder apparatus to work under pressure upto 27 kbar at temperatures upto 350°C and external heating of the high pressure cell [10] (Fig.2). The displacement of the piston is measured by micrometer. Error coming from distortion of various parts of the apparatus is eliminated by making the method differential, taking the difference of displacement for the material under investigation and empty cell. Pressure is calibrated volumetrically on the basis of known phase transitions NH_4F I-II-III, BiI-BiII-BiIII, CeII-CeIV, CsI-CsII and compressibilities of different metals.

The accuracy of pressure determination is 0.14-0.5 kbar, volume - 0.07-0.20% (in an absolute sense $\pm 10^{-3}$ in V/V_0). The distortion- and friction-corrected experimental results for a given sample consist of a set of P-V isotherms.

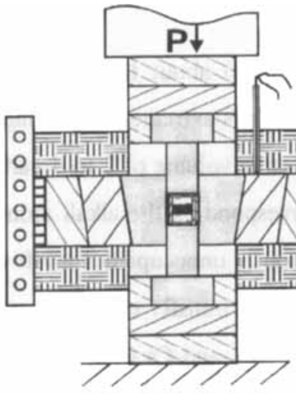

FIGURE 2 Piston-cylinder high pressure apparatus with the external heating of the cell and volumetric control of the reaction

The piston cylinder apparatus was also used in a modification with the internal heating of the cell (Boyd-England construction [23]), which extends the temperature limits upto 1000°C, but decreases the accuracy of the piston displacement measurements due to the irreproducible deformations of the pyrophyllite cell.

The possibility to study the reactions *in situ* reviled the following striking features of the high pressure metal intercalation:

- the reactions under pressure proceed very *rapidly*. For the heavy alkali metals the synthesis time is an order of a minutes or even seconds. Li and Na intercalation into graphite, fullerene and carbon nanotubes proceeds more slowly (0.5-4 hours depending on carbon type, sizes of the sample, etc.) but is much more rapid than under traditional conditions and takes place at lower temperatures. The temperature factor is quite important in case of Li-carbon compounds, as high temperature synthesis leads to the formation of parasitic. lithium carbide;

- for the heavy alkali metals the reaction proceeds in *solid phase*, i.e. below the melting point of alkali metal at given pressure.

RESULTS - DISCUSSION

What is so exciting (curious) about the compounds obtained? Atomic alkali metal density in MC_{2-4} GICs is extremely high - higher than in pure metal (!) in spite of presence in the same volume of 2 to 4 carbon atoms per 1 metal (Table 3). These densities correspond to the alkali atom compression $V/V_0 < 0.5$. Compression causes previously unoccupied d levels of alkali metal to drop below the Fermi level, leading to a transfer of electrons from s to d states [1]. Thus under the compression K, Rb, and Cs transform to metals that have a d^1 electron configuration, becoming transition metal-like. The atomic radius decreases dramatically at the transition as s electrons are transferred to the spatially more localized d states. It should be noted that s-d transfer results in a redistribution of charge in a way typical for a partly covalent character of the bonds [24]. For Li the compression leads to the increase of 2p states occupancy [25]. It is significant that Li metal and Li clusters have already quite high contribution of 2p electrons at zero pressure (Fig.3).

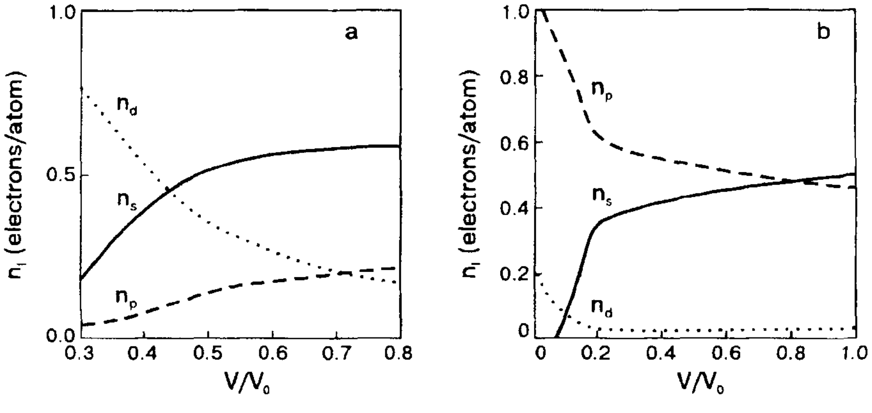

FIGURE 3 Projected numbers of state at E_F for 6s, 6p and 5d-e of Cs (a) [26]; and 2s, 2p and 3d for Li (b) [25] as a function of compression

TABLE 3 Alkali metal density in pristine metal and graphite intercalation compounds (g of metal per 1 cm^3 of the compound)

in GICs		Crystalline metal	
LiC_2	0.59	Li	0.53
KC_4	1.15	K	0.86
RbC_4	2.39	Rb	1.53
CsC_4	3.52	Cs	1.90

To understand the nature of bonding in superdense alkali metal compounds the complex investigation of their electronic and crystalline structure has been undertaken for the last years [9,27-32]. These investigations have shown:

- The presence of superdense structural fragments (metal clusters) with very short M...M distances in high pressure GICs (fig.4) [9,27]. LiC_x high pressure compounds contain 7-atomic hexagonal Li clusters (of D_{6h} symmetry) with 2.49 Å Li-Li distances. CsC_4 structure contains Cs atom chains with Cs...Cs distances along the chain 2.48 Å, so in fact linear Cs clusters. The presence of the dense alkali metal clusters in the layers was also proved by IR- and NMR-spectroscopies [28,29]. K and Rb MC_4 compounds also form dense metal monolayers, but their stability is much less than that of CsC_4 and LiC_2.

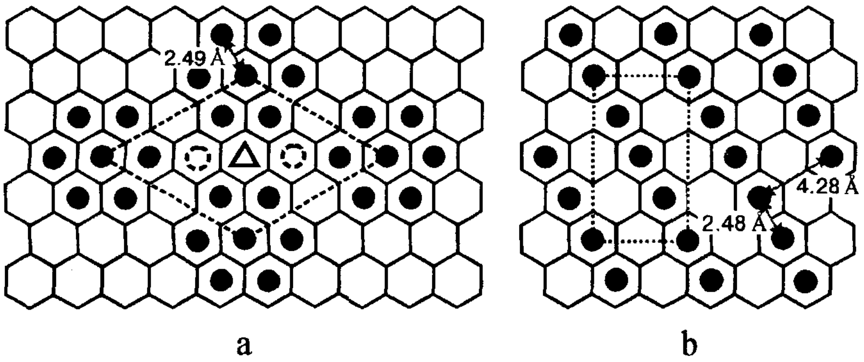

FIGURE 4 LiC_x (Li_7C_{24}-○, Li_9C_{24}-○+Δ) (a) and CsC_4 (b) in-plane structures.

- Decrease of metal - to - graphite charge transfer (per metal atom) in superdense compounds compare to normal ones. It follows from C-C in-plane distances, which are sensitive to the charge transfer to the conducting band of graphite (LiC_6 - 1.436, $LiC_{2.2}$ - 1.433, CsC_8 - 1.431, CsC_4 - 1.427 Å) [9,27], Auger spectroscopy on cesium compounds [30], XPS investigations [31], ^7Li NMR Knight shift [29]. So the electronic density is partially localized on the metal-like states. Therefore the short M-M distances observed in these compounds may be explained by the presence of covalent M-M bonding in the alkali metal layers due to the electron transfer from *ns* to much more localized *np* (in case of Li) or *(n-1)d* states and the overlapping of these orbitals with high angular momentum. This type of bonding is observed in pristine alkali metals at high pressures [24,26] and in metal clusters as well [33].
- According to their stability alkali metal GICs may be arranged as follows: $LiC_2 \sim CsC_4 > RbC_4 > KC_4 >> NaC_{2\text{-}3}$ (Table 2). Decrease of the stability and increase of the synthesis pressure in this range may be explained by the increase of the s-to-d transition energy in the range Cs→Rb→K and thus the increase of the energy required to produce and stabilize the metal superdense state. Na has no d states close to the Fermi level E_F which explains the stability of bcc phase and the absence of phase transitions in Na under pressure up to at least 350 kbar (up to 1 Mbar according to the theoretical calculations) [34]. This fact may explain the difficulty to obtain and stabilize superdense Na in graphite matrix. Li apparently uses its 2p states, which becomes more favorable under compression [25] and under influence of aromatic ligand [35,36], to form covalent Li clusters.
- The ability of aromatic carbon matrix to stabilize superdense alkali metal state. Quantum chemical calculations show that aromatic carbon matrix works in the same direction as high pressure with respect to the alkali metal states [36], lowering the states with high angular momentum (d,p), which can provide the stabilization effect of aromatic carbon. Experimentally it was shown that

modification of the matrix itself (boronation) can stabilize Li - graphite compounds at very high Li densities - $LiC_{2.18}$ [37]. Very recently the possibility for alkali metals to imitate transition metals under pressure has been also shown by L.J. Parker et al [2] in Pennsylvania State University in their investigations of K- Ni system under pressure. In this case alkali metal under pressure also possesses transition metal-like d^1 configuration and forms direct bonding with Ni, but contrarily to carbon (graphite) interaction with Ni can not stabilize this state.

So we believe that superdense alkali metal clusters are stabilized by the covalent M-M bonding in the layer on one hand and by the interaction with aromatic carbon on the other.

- Li state in Li-nanotubes compounds is hardly investigated as yet. Nevertheless according to the IR spectroscopy data it is very similar to that in graphite. Li and Na in fullerene lattice form 3D clusters which implyes very short M-M distances and high degree of covalence.

CONCLUSION

Combination of the high pressure and presence of aromatic carbon matrix leads to: (1) decrease of s-to-d transition pressure in alkali metals; (2) stabilization of the superdense metal clusters under ambient conditions. The stabilization effect:

first, allows to study the superdense alkali metals under ambient conditions (the compression of alkali metal in graphite matrix is equivalent to that of crystalline metals under pressures 100-500 kbar) which can be of particular interest in solid state physics and chemistry, and also in the related fields of geology dealing with superdense matter in the Earth core;

second, gives interesting opportunities with regard to the applied materials, especially as a storage material (high capacity alkali metal materials). *Thus dense lithium compounds promise extraordinary* high energy density for batteries and weight elimination for portable electronics. In fact the Li atomic density is 10% greater in LiC_2 obtained under pressure than in crystalline Li in spite of the presence in the same volume of carbon. The primary capacity of this material was shown to be nearly three times higher than that of LiC_6 [38]. These materials can be exploited both for the primary (non-rechargeable) and secondary batteries due to the good intercalation reversibility (though with lower capacity than the primary one).

References

[1.] A.K. McMahan, *Phys. Rev. B*, **17**, 1521 (1978); K. Takemura, K. Syassen, *Phys. Rev. B*, **32**, 2213 (1985); W. Zittel, J. Meyer-ter-Vehn, J. Kubler, *Solid State Commun.*, **62**, 97 (1987); K. Takemura, O. Shimomura, H. Fujihisa, *Phys. Rev. Lett.*, **66**, 2014 (1991).

[2.] L.J. Parker, T. Atou, and J.V. Badding, *Science*, **273**, 95 (1996).

[3.] R. Clarke, N. Wada, S.A. Solin, *Phys. Rev. Lett.*, **44**, 1616 (1980); N. Wada, R. Clarke, S.A. Solin, *Synth. Met.*, **2**, 27 (1980); N. Wada, S.A. Solin, *Physica B*, 105, 268 (1981).

[4.] C.D. Fuerst, D. Moses, J.E. Fischer, *Phys. Rev. B*, **24**, 7471 (1981); J.E. Fischer, C.D. Fuerst, K.C. Woo, *Synth. Met.*, **7**, 1 (1983); H.J. Kim, J.E. Fischer, D.B. McWhan, J.D. Axe, *Phys. Rev. B*, **33**, 1329 (1986).

[5.] D. Guerard and A. Herold, *C.R. Acad. Sc. Paris*, **275C**, 571 (1971); *Carbon*, **13**, 337 (1975).

[6.] K.N. Semenenko, V.V. Avdeev, V.Z. Mordkovich, *Dokl. AN SSSR*, **271**, 1402 (1983); *Zh. Neorg. Khim.*, **29**, 2236 (1984).

[7.] V.A. Nalimova, V.V. Avdeev, I.A. Udod, and K.N. Semenenko, *Zh. Obsch. Khim.*, **60**, 868 (1990).

[8.] I.T. Belash, A.D. Bronnikov, O.V. Zharikov, and A.V. Palnichenko, *Solid State Commun.*, **69**, 921 (1989).

[9.] V.A. Nalimova, D. Guerard, M. Lelaurain, O.V. Fateev, *Carbon*, **33**, 177 (1995); D.Guerard and V.A. Nalimova, *Mol. Cryst. Liq. Cryst.*, **244**, 263 (1994).

[10.] V.V. Avdeev, V.A. Nalimova, and K.N. Semenenko, *Dokl. AN SSSR*, **297**, 361 (1987); ibid, **304**, 111 (1989); *High Pressure Res.*, **6**, 11 (1990).

[11.] V.V. Avdeev, O.V. Zharikov, V.A. Nalimova, A.V. Palnichenko, and K.N. Semenenko, *Lett. J. Exp. Theor. Phys.*, **43**, 376 (1986).

[12.] K. Syassen, R. Sonnenschein, M. Hanfland, and H.J. Beister, *Synth. Met.*, **34**, 293 (1989).

[13.] V.A. Nalimova, S.N. Chepurko, V.V. Avdeev, and K.N. Semenenko, *Synth. Met.*, **40**, 267 (1991).

[14.] I.T. Belash, A.D. Bronnikov, O.V. Zharikov, and A.V. Palnichenko, *Solid State Commun.*, **64**, 1445 (1987).

[15.] V.A. Nalimova, V.V. Avdeev, and K.N. Semenenko, *Dokl. AN SSSR*, **315**, 620 (1990).

[16.] I.A. Udod and V.K. Genchel, *High Pressure Res.*, **8**, 581 (1992).

[17.] V.A. Nalimova, A.P. Zakharov, V.V. Avdeev, and K.N. Semenenko, *Synth. Met.*, **48**, 247 (1992).

[18.] S. Menu, L. Duclaux, J. Conard, P. Lauginie, and V.A. Nalimova, *J. Phys. Chem. Solids*, **57**, 967 (1996).

[19.] V.A. Nalimova, D.E. Sklovsky, H. Alvergnat-Gaucher, S. Bonnamy, F. Beguin, *Accepted to Synth. Met.*, 1997.

[20.] I.O. Bashkin, V.I. Rashchupkin, A.F. Gurov, A.P. Moravsky, O.G. Rybchenko et al, *J.Phys.: Condens. Matter*, **6**, 7491 (1994); V.D. Blank, S.G. Buga, N.R. Serebryanaya, G.A. Dubitsky, S.N. Sulyanov et al, *Phys. Lett. A*, **220**, 149 (1996); A.M. Rao, P.C. Eklund, U.D. Venkateswaran, J. Tucker, M.A. Duncan et al, *Appl. Phys. A*, **64**, 231 (1997).

[21.] A.D. Bozhko, D.E. Sklovsky, and V.A. Nalimova, to be published.

[22.] S.K. Konovalov and B.M. Bulichev, *Inorg. Chem.*, **34**, 172 (1995).

[23.] F.R. Boyd and J.L. England, *J. Geophys. Res.*, **65**, 741 (1960).

[24.] S.G. Louie and M.L. Cohen, *Phys. Rev. B*, **10**, 3237 (1974).

[25.] J.C. Boettger and R.C. Albers, *Phys. Rev. B*, **39**, 3010 (1989).

[26.] D. Glotzel, A.K. McMahan, *Phys. Rev. B*, **20**, 3210 (1979).

[27]. C. Bindra, V.A. Nalimova, and J.E. Fischer, *present Symposium*.

[28.] V.A. Nalimova, G.N. Bondarenko, V.L. Kofman, V.V. Avdeev, K.N. Semenenko, 20th Biennial Conference on Carbon, Santa Barbara, June 23-28, 1991, p.684; G.N. Bondarenko, V.A. Nalimova, O.V. Fateev, D. Guerard, K.N. Semenenko, *Submitted to Carbon*.

[29.] J. Conard. V.A. Nalimova, and D. Guerard, *Mol. Cryst. Liq. Cryst.*, **245**, 25 (1994).

[30.] V.A. Nalimova, V.V. Avdeev, K.N. Semenenko, N.R. Gall, S.N. Mikhailov, E.V. Rut'kov, and A. Tontegode, *Synth. Met.*, **46**, 79 (1992).

[31.] V.Z. Mordkovich, *Synth. Met.*, **80**, 243 (1996).

[32.] C. Bindra, V.A. Nalimova, D.E. Sklovsky, and J.E. Fischer, *Submitted to Phys. Rev. B*.

[33.] H.O. Beckmann, J. Koutecky, P. Botschwina, W. Meyer, *Chem. Phys. Lett.*, **67**, 119 (1979); P. Fantucci, J. Koutecky, G. Pacchioni, *J. Chem. Phys.*, **80**, 325 (1984); D.A. Garland, D.M. Lindsay, *J.Chem.Phys.*, **80**, 4761 (1984).

[34.] K. Takemura, K. Syassen, *Phys. Rev. B*, **28**, 1193 (1983).

[35.] E. Weiss, A.C. Lucken, *J. Organomet. Chem.*, **2**, 197 (1964); C. Krueger, Yi-Hung Tsay, *Angew. Chem.*, **85**, 105 (1973).

[36.] A.Yu. Ermilov, *Ph. D. Thesis*, Moscow State University, 1997.

[37.] V.A. Nalimova, C. Bindra, J.E. Fischer, *Solid State Commun.*, **97**, N 7, 583 (1996).

[38.] C. Bindra, V.A. Nalimova, D.E. Sklovsky, Z. Benes, J.E. Fischer, *Submitted to J. Electrochem. Soc.*