

# Structural stability of the rhombohedral 2D polymeric phase of $C_{60}$ studied by in-situ Raman scattering at pressures up to 30 GPa

K.P. Meletov<sup>a,b</sup>, J. Arvanitidis<sup>a,c</sup>, G.A. Kourouklis<sup>a,\*</sup>, K. Prassides<sup>c</sup>,  
Y. Iwasa<sup>d,e</sup>

<sup>a</sup> Physics Division, School of Technology, Aristotle University of Thessaloniki, GR-540 06 Thessaloniki, Greece

<sup>b</sup> Institute of Solid State Physics of the Russian Academy of Sciences, 142432 Chernogolovka, Moscow region, Russia

<sup>c</sup> School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton BN1 9QJ, UK

<sup>d</sup> Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

<sup>e</sup> CREST, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan

Received 11 March 2002; in final form 25 March 2002

## Abstract

The structural stability of the rhombohedral two-dimensional (2D) polymeric phase of  $C_{60}$  has been studied as a function of pressure up to  $\sim 30$  GPa at room temperature by means of in-situ Raman scattering. An irreversible transformation to a new disordered phase was observed at a pressure of  $\sim 15$  GPa. The intensity of the  $A_g(2)$  pentagonal pinch (PP) mode rapidly decreases in the pre-transitional pressure range while the Raman spectrum of the transformed material becomes very diffuse. The high-pressure phase recovered to normal conditions is metastable and transforms under heating to a mixture of pristine and dimerized  $C_{60}$  as can be seen by their Raman spectra. The retention of the fullerene molecular cage at high pressure and quenching of the PP-mode are the indications that the high-pressure phase may be associated with a random creation of new polymeric bonds between the molecules in adjacent polymeric planes of the 2D-rhombohedral phase of  $C_{60}$ . © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Pristine  $C_{60}$  has a great potential for polymerization due to the existence of 30 double C=C bonds in the fullerene molecular cage. The photo-

polymerization of  $C_{60}$  was observed, for the first time, under intense illumination by light and the so-called [2+2] cyclo-addition mechanism was proposed to explain the creation of covalent polymeric bonds among adjacent fullerene molecules [1]. The treatment of  $C_{60}$  under various conditions of high pressure and high temperature also results in the formation of polymeric networks of various dimensionalities based on the  $C_{60}$  molecular cage [2–5]. The crystal structures of the

\* Corresponding author. Fax: +30-31995928.

E-mail address: gak@vergina.eng.auth.gr (G.A. Kourouklis).

polymeric phases have been identified as one-dimensional (1D) orthorhombic, two-dimensional (2D) tetragonal, 2D-rhombohedral and three-dimensional (3D) face-centered cubic [2–4]. The infrared absorption and Raman scattering spectra of these polymeric phases, as well as their crystal structure were studied in detail for samples prepared under carefully controlled conditions of high pressure and high temperature treatment [6]. In addition, the treatment of fullerite under highly non-uniform pressure and high temperature results in the production of several disordered polymeric phases, the so-called hard fullerite phases, which have also 3D polymeric character [7–9].

The polymerization of  $C_{60}$  is characterized by the destruction of a number of double  $C=C$  bonds and the creation of intermolecular covalent bonds associated with  $sp^3$ -like fourfold coordinated carbon atoms in the fullerene molecular cage. Their number increases from 4 to 8 and to 12 per cage for 1D-orthorhombic, 2D-tetragonal and 2D-rhombohedral polymeric phases, respectively and it is expected to increase further in the 3D-polymeric phases. Theoretical studies by Okada et al. [10] have predicted the formation of a three-dimensionally polymerized metallic fullerite phase having 24  $sp^3$ -like hybridized carbon atoms per  $C_{60}$  cage, by uniaxial compression at a pressure of  $\sim 20.2$  GPa, perpendicular to the polymeric sheets of the 2D-tetragonal polymeric phase of  $C_{60}$ . Another theoretical study, by Burgos et al. [11], predicted that uniaxial compression perpendicular to the chains in the 1D or to the polymeric planes in the 2D polymeric phases of  $C_{60}$  leads to 3D polymerization with 52, 56 and even 60  $sp^3$ -like coordinated carbon atoms per fullerene molecular cage. These transformations are expected to take place at pressures lower than 14 GPa and the new phases are semiconducting with large bulk and shear moduli.

Recent experimental Raman studies of the pressure behavior of the 2D-tetragonal polymeric phase of  $C_{60}$  [12,13] have revealed prominent irreversible changes in the Raman spectra of this material near 20 GPa, related most likely to its further polymerization in accordance with the theoretical prediction of Okada et al. [10]. In this Letter we report the results of our studies on the

2D-rhombohedral polymeric phase of  $C_{60}$  to pressure up to  $\sim 30$  GPa by means of in-situ Raman scattering using the diamond anvil cell (DAC) technique. Our study is focused principally on the structural stability and the pressure-induced transformations of the 2D-rhombohedral polymeric phase, and on the comparison between experimental results and theoretical predictions [10,11].

## 2. Experimental

The 2D polymerized  $C_{60}$  was obtained by subjecting 99.99% pure pristine  $C_{60}$  powdered material to a pressure of  $P \approx 5$  GPa at a temperature of 773 K. The X-ray analysis, after the high-pressure treatment, confirmed that the crystal structure of the polymer is rhombohedral (space group:  $R\bar{3}m$ ,  $a = 9.22$  Å and  $c = 24.6$  Å) [2]. The samples used for the high pressure measurements had dimensions of  $\sim 100$   $\mu\text{m}$  and have been selected from the batch material by means of micro-Raman probing for their intense, clear and spatially uniform Raman response, typical of the 2D-rhombohedral polymeric phase [6].

Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen cooled detector system. The spectra were taken in the back-scattering geometry by the use of the micro-Raman system comprising an OLYMPUS microscope equipped with objective of  $20\times$  magnification and a spatial resolution of  $\sim 8$   $\mu\text{m}$ . The spectral width of the system was  $\sim 6$   $\text{cm}^{-1}$ . The 514.5 nm line of an  $\text{Ar}^+$  laser with beam power below 10 mW, measured before the cell, was used for excitation. Measurements of the Raman spectra at high pressures were carried out using a DAC of Mao-Bell type [14]. The 4:1 methanol-ethanol mixture was used as pressure transmitting medium and the ruby fluorescence technique was used for pressure calibration [15].

## 3. Results and discussion

The Raman spectra of the 2D-rhombohedral polymeric phase of  $C_{60}$ , in the frequency region

100–2000  $\text{cm}^{-1}$  and for pressure up to  $\sim 30$  GPa, are illustrated in Fig. 1. The spectra were recorded upon pressure increase, while the spectral region around the significantly strong triply degenerate  $T_{2g}$  mode of diamond, appearing at 1332  $\text{cm}^{-1}$  at ambient pressure [16], is excluded. The background, which is gradually increasing with pressure, is subtracted from the experimental spectra. The initial spectrum taken at  $\sim 0.9$  GPa exhibits all the typical Raman features of this material and is identical with the spectra reported earlier at ambient conditions [6]. The vertical lines, in Fig. 1, indicate some peaks related to the presence of oligomers in the material, while arrows indicate three methanol–ethanol mixture

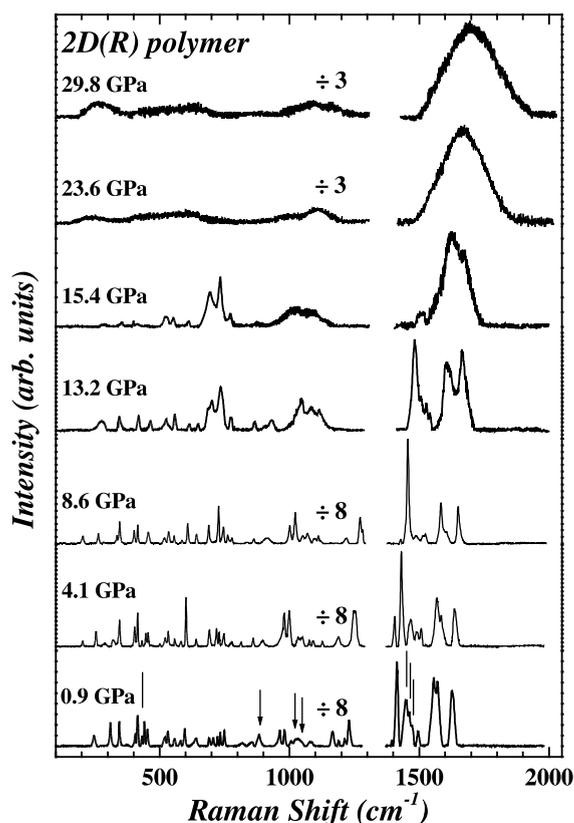


Fig. 1. Raman spectra of the 2D-rhombohedral polymeric phase of  $C_{60}$  at room temperature and various pressures, recorded upon pressure increase. The vertical lines indicate peaks related to the presence of oligomers in the material while vertical arrows indicate methanol–ethanol mixture peaks.

peaks. The Raman spectrum of the polymer is richer in structure than that of pristine  $C_{60}$  due to the splitting of the Raman active fivefold degenerate  $H_g$  phonon modes and/or to the activation of silent modes. As the pressure increases, the Raman peaks shift to higher energies and their bandwidth gradually increases. The broadening of the Raman peaks is further enhanced above 10 GPa most probably due to the solidification of the pressure-transmitting medium. It is known that the methanol–ethanol mixture is fully hydrostatic up to 10 GPa while in its glassy form could support as high as 0.4 GPa gradient at extreme pressures [17], therefore we expect shear components in the order of this gradient. Significant changes are first observed at pressure higher than  $\sim 15$  GPa when the Raman spectrum becomes very diffuse and loses its fine structure in all frequency regions. This transformation is preceded by a rapid decrease in the intensity of the  $A_g(2)$  ‘pentagonal pinch’ (PP)-mode and a relative increase in the intensities of the split  $H_g(8)$  and  $G_g(6)$  modes. The frequencies, the assignment and the pressure coefficients of the Raman-active phonon modes of the 2D-rhombohedral phase of  $C_{60}$  are shown in Table 1. The Raman spectra at pressure higher than  $\sim 15$  GPa differ drastically from the initial spectrum of the 2D-rhombohedral phase due to considerable broadening of the Raman peaks, while the relative intensity distribution among the various phonon bands is preserved. The broad Raman features above  $P \geq 15$  GPa, designated as  $\Omega(1)$ – $\Omega(9)$  in Table 1 (see also Fig. 2), can be tracked back to 2D-rhombohedral phase and seem to incorporate the corresponding group of the well resolved Raman peaks of the 2D-rhombohedral phase. Comparing the Raman spectrum of the high-pressure phase to that of the high-pressure phase of the 2D-tetragonal polymeric phase of  $C_{60}$  [12,13], we observe that the former does not contain peaks at high energy like the 1840  $\text{cm}^{-1}$  peak. In addition, the transformed phase shows a spatially uniform Raman response over all the surface of the sample, as it was evidenced by probing various places in the sample, a behavior which differs drastically from the 2D-tetragonal polymeric phase of  $C_{60}$  [13].

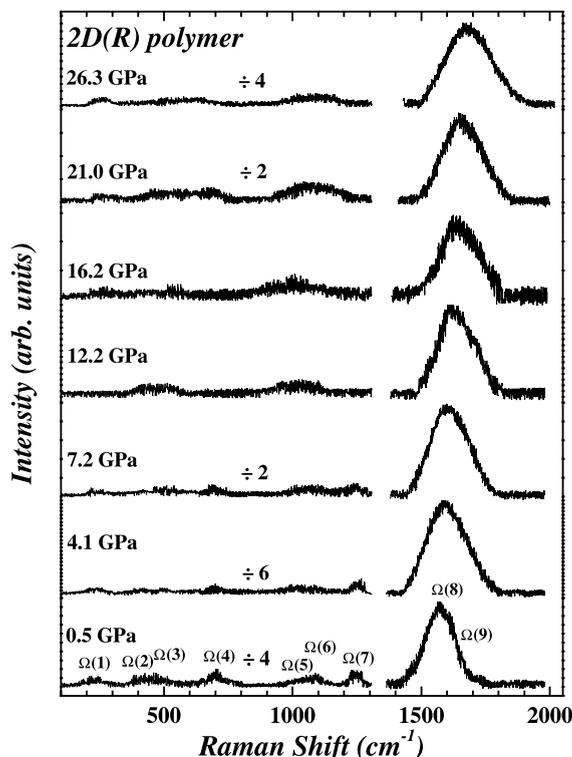


Fig. 2. Raman spectra of the 2D-rhombohedral polymeric phase of  $C_{60}$  at room temperature and various pressures, recorded upon pressure decrease.

Fig. 2 shows the Raman spectra of the polymer upon pressure release. The decrease of pressure from  $\sim 30$  GPa down to ambient pressure results in the gradual shift of the Raman peaks to lower energies without any other observable changes in the Raman intensity distribution. The high-pressure phase remains stable down to ambient conditions. Note that this downstroke cycle in pressure lasted a long period of time ( $\sim$  one month). The total number of peaks, their positions and the pressure coefficients of the recovered high-pressure phase are quite different from those of the initial 2D-rhombohedral phase (see Table 1). The recovered sample was tested by means of micro-Raman probing at various sites in order to check the uniformity of its structure. The Raman spectra recorded from several sites are identical and show the same diffuse Raman bands, indicating that the high-pressure phase of the material is highly uni-

form. Despite the similarities in the diffused Raman bands, the high-pressure phase differs significantly from that of the amorphous carbon with respect to both the number of peaks and their location. Our observations from several pressure runs show that the recovered sample is in a rather stable phase which does not change at ambient conditions, at least for a period over one week. To reveal the possible contribution of the pressure-induced imperfections and structural defects in the broadening of the Raman bands, we have annealed the recovered samples under various temperature conditions. The Raman spectra of the annealed samples show that the material undergoes some transformation when subjected to a temperature higher than  $300^\circ\text{C}$ . The results of the micro-Raman probing of the recovered sample at ambient conditions before and after annealing are presented in Fig. 3b,c, respectively, along with the initial spectrum of the 2D-rhombohedral phase (Fig. 3a). All the spectra in Fig. 3 were recorded in the  $1350\text{--}1800\text{ cm}^{-1}$  energy region, which contains the most intense Raman peaks. The Raman spectrum of the annealed material is spatially uniform and differs considerably from that of the high-pressure phase as well as that of the initial 2D-rhombohedral polymeric phase. This spectrum contains a relatively narrow and intense Raman band near  $1464\text{ cm}^{-1}$ , related to the PP-mode in the case of a mixture, containing monomers and dimers of  $C_{60}$ , and is similar to the spectra of various annealed polymeric phases of  $C_{60}$  [5,12].

Our experimental data provide a strong indication that the 2D-rhombohedral polymeric phase of  $C_{60}$  undergoes an irreversible transformation at  $P > 15$  GPa. The initial well resolved Raman spectrum of the 2D (R) polymeric phase transforms to a diffuse one that is typical of a disordered phase. The rapid decrease of the  $A_g(2)$  mode intensity and the enhancement of the neighboring  $H_g(8)$  and  $G_g(6)$  modes in the pre-transitional pressure range is reminiscent of analogous behavior exhibited by these modes in the 2D-tetragonal polymeric phase of  $C_{60}$  before its further polymerization under high pressure [12,13]. Taking into account that the PP-mode is associated with the in-phase stretching vibrations of the double  $\text{C}=\text{C}$  bonds, the decrease of its intensity

Table 1

Phonon frequencies and their pressure coefficients for the initial 2D-rhombohedral polymeric phase of C<sub>60</sub> and the resulting 'high-pressure' phase

Rhombohedral 2D polymeric C <sub>60</sub>			'High-pressure' phase		
Mode <sup>a</sup>	$\omega_i$ (cm <sup>-1</sup> )	$\partial\omega_i/\partial P$ (cm <sup>-1</sup> /GPa)	Mode	$\omega_i$ (cm <sup>-1</sup> )	$\partial\omega_i/\partial P$ (cm <sup>-1</sup> /GPa)
H <sub>g</sub> (1)	245	2.3	Ω(1)	228	1.3
H <sub>g</sub> (1)	267	2.8			
H <sub>g</sub> (1)	308	3.4			
H <sub>u</sub> (1)	342	0.6			
F <sub>2u</sub> (1)	366	1.3	Ω(2)	397	3.1
G <sub>u</sub> (1)	406	-0.4			
H <sub>g</sub> (2)	415	0.2			
H <sub>g</sub> (2)	438	2.2			
H <sub>g</sub> (2)	451	0.9	Ω(3)	470	4.7
A <sub>g</sub> (1)	492	1.1			
F <sub>1u</sub> (1)	520	0.1			
F <sub>2g</sub> (1)	532	0.3			
F <sub>1g</sub> (1)	558	-0.2			
H <sub>u</sub> (2)	579	0.8			
H <sub>u</sub> (2)	596	1.4			
H <sub>u</sub> (3)	640	0.4			
H <sub>g</sub> (3)	695	-0.5	Ω(4)	705	-0.8
F <sub>2u</sub> (2)	709	-0.6			
H <sub>g</sub> (3)	712	1.8			
H <sub>g</sub> (3)	731	-0.2			
H <sub>g</sub> (4)	749	-0.2			
H <sub>g</sub> (4)	749	1.8			
F <sub>2g</sub> (2)	767	0.4			
H <sub>g</sub> (4)	776	0.3			
F <sub>2u</sub> (3)	827	1.0			
H <sub>u</sub> (4)	856	0.8			
H <sub>u</sub> (4)	868	0.6			
G <sub>g</sub> (2)	958	5.0			
F <sub>1g</sub> (2)	977	5.4			
F <sub>2u</sub> (4)	1016	2.9	Ω(5)	1025	-1.4
F <sub>2u</sub> (4)	1037	2.4			
H <sub>g</sub> (5)	1042	8.8			
H <sub>g</sub> (5)	1078	3.9	Ω(6)	1086	0.3
H <sub>g</sub> (5)	1109	4.2			
G <sub>g</sub> (3)	1158	7.2			
G <sub>g</sub> (3)	1195	-0.5			
F <sub>2g</sub> (3)	1204	9.4			
H <sub>g</sub> (6)	1224	5.8			
H <sub>g</sub> (6)	1230	6.2	Ω(7)	1244	0.6
H <sub>g</sub> (6)	1260	-			
G <sub>g</sub> (4)	1314	-			
H <sub>g</sub> (7)	1385	5.4			
A <sub>g</sub> (2)	1410	5.6			
F <sub>1g</sub> (3)	1495	3.5			
H <sub>g</sub> (8)	1554	3.7			
H <sub>g</sub> (8)	1563	3.9	Ω(8)	1568	4.3
H <sub>g</sub> (8)	1569	4.3			
G <sub>g</sub> (6)	1621	3.6			
G <sub>g</sub> (6)	1627	3.8	Ω(9)	1638	3.3

<sup>a</sup> The mode assignment for the initial 2D (R) polymeric phase refers to the irreducible representations of the C<sub>60</sub> molecule [18] and follows in general that of [6].

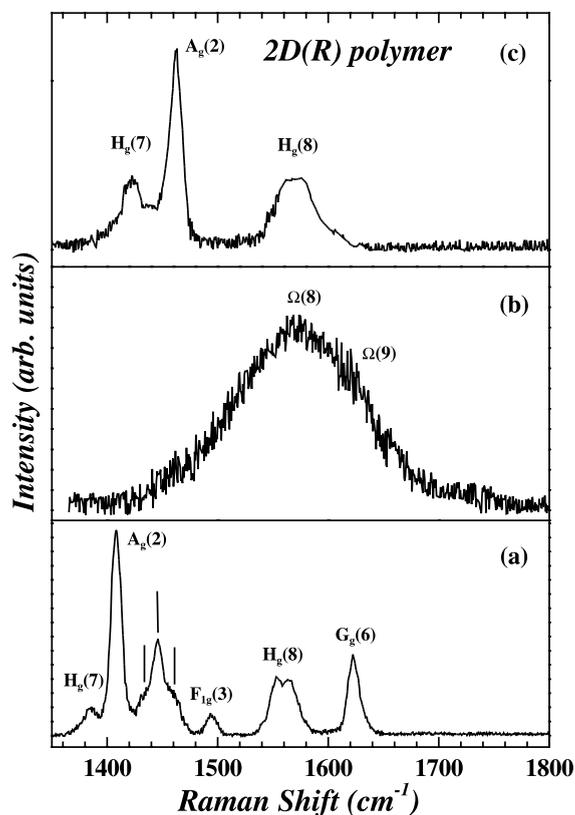


Fig. 3. Raman spectra of the initial 2D-rhombohedral polymeric phase of  $C_{60}$  and of the recovered sample after pressure release in the frequency region  $1350\text{--}1800\text{ cm}^{-1}$ , recorded at ambient conditions. (a) The initial 2D (R) polymeric phase. The vertical lines indicate peaks related with the presence of oligomers in the material. (b) The 'high-pressure' phase of the polymer. (c) The Raman spectrum of the 'high-pressure' phase after being annealed at  $\sim 600\text{ K}$  and at ambient pressure. The spectrum consists mainly of  $C_{60}$  monomers and dimers.

may be related to the destruction of some of these bonds and subsequent creation of covalent links between molecules belonging to adjacent planes. Similar behavior of the  $A_g(2)$  PP-mode was observed in various polymeric phases of  $C_{60}$  characterized by different numbers of  $sp^3$ -like fourfold coordinated carbon atoms per  $C_{60}$  molecule [3,5,6]. Even though pressure decreases preferentially the interplane distance in the polymer,  $C_{60}$  molecular cages belonging to adjacent polymeric planes of the 2D-rhombohedral phase do not have relative orientations which are optimal for the formation

of interplane covalent bonds. Therefore we may assume that the new bonds are formed in a random way due to some distortion in the molecular orientations. As a result, the new high-pressure phase exhibits a degree of disorder characterized by a random out-of-plane polymerization. Note that this behavior differs significantly from that of the 2D-tetragonal polymeric phase of  $C_{60}$ , in which the pressure-induced shortening of the intermolecular distances, accompanied by the optimal orientation of molecules, leads to a high degree of regularity in the formation of the out-of-plane covalent bonds. This regularity in the interplane bonding is manifested in the Raman spectra of the high-pressure phase of the 2D (T) polymer giving well resolved and rich Raman spectra [10,12,13].

In the 2D (R) polymer the diffuse Raman spectrum of the high-pressure phase may be related to a disordered polymeric phase of  $C_{60}$  characterized by random covalent bonding between molecules belonging to adjacent 2D-polymeric planes of the initial rhombohedral phase. This conclusion is supported by the retention of the fullerene molecular cage in the high-pressure phase as well as by the similarity in the pre-transitional behavior with that of the 2D-tetragonal polymeric phase of  $C_{60}$ . The experimentally observed pressure behavior of the 2D-rhombohedral polymeric phase of  $C_{60}$  is not in step with the theoretical calculations reported in [11] which predict regular covalent bonding between the polymeric sheets under pressure.

Finally, we note that a detailed study of the high-pressure behavior of the 2D-rhombohedral polymeric phase of  $C_{60}$  by means of in-situ X-ray diffraction measurements under pressure and/or X-ray diffraction study of the recovered sample, would be necessary in order to elucidate further the nature of the observed phase transition and the properties of the high-pressure phase.

#### Acknowledgements

The support by the General Secretariat for Research and Technology, Greece, is acknowledged. This research has been also supported by a

Marie Curie Fellowship of the European Community programme 'Improving the Human Research Potential' to JA under contract number HPMF-CT-2001-01436, the NEDO Frontier Carbon Technology and the Royal Society (UK/Japan CRP).

## References

- [1] A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, *Science* 259 (1993) 955.
- [2] Y. Iwasa, T. Arima, R.M. Fleming, T. Siegrist, O. Zhou, R.C. Haddon, L.J. Rothberg, K.B. Lyons, H.L. Carter Jr., A.F. Hebard, R. Tycko, G. Dabbagh, J.J. Krajewski, G.A. Thomas, T. Yagi, *Science* 264 (1994) 1570.
- [3] M. Nunez-Regueiro, L. Marques, J.-L. Hodeau, O. Bethoux, M. Perroux, *Phys. Rev. Lett.* 74 (1995) 278.
- [4] V.V. Brazhkin, A.G. Lyapin, S.V. Popova, *JETP Lett.* 64 (1996) 802.
- [5] B. Sundqvist, *Adv. Phys.* 48 (1999) 1.
- [6] V.A. Davydov, L.S. Kashevarova, A.V. Rakhmanina, V.M. Senyavin, R. Ceolin, H. Szwarc, H. Allouchi, V. Agafonov, *Phys. Rev. B* 61 (2000) 11936.
- [7] V.D. Blank, M.Yu. Popov, S.G. Buga, V. Davydov, V.N. Denisov, A.N. Ivlev, B.N. Mavrin, V. Agafonov, R. Ceolin, H. Szwarc, A. Rassat, *Phys. Lett. A* 188 (1994) 281.
- [8] L. Marques, M. Mezouar, J.-L. Hodeau, M. Nunez-Regueiro, N.R. Serebryanaya, V.A. Ivdenko, V.D. Blank, G.A. Dubitsky, *Science* 283 (1999) 1720.
- [9] L.A. Chernozatonskii, N.R. Serebryanaya, B.N. Mavrin, *Chem. Phys. Lett.* 316 (2000) 199.
- [10] S. Okada, S. Saito, A. Oshiyama, *Phys. Rev. Lett.* 83 (1999) 1986.
- [11] E. Burgos, E. Halac, R. Weht, H. Bonadeo, E. Artacho, P. Ordejon, *Phys. Rev. Lett.* 85 (2000) 2328.
- [12] K.P. Meletov, S. Assimopoulos, I. Tsilika, G.A. Kourouklis, J. Arvanitidis, S. Ves, B. Sundqvist, T. Wägberg, *Chem. Phys. Lett.* 341 (2001) 435.
- [13] K.P. Meletov, J. Arvanitidis, I. Tsilika, S. Assimopoulos, G.A. Kourouklis, S. Ves, A. Soldatov, K. Prassides, *Phys. Rev. B* 63 (2001) 054106.
- [14] A. Jayaraman, *Rev. Sci. Instrum.* 57 (1986) 1013.
- [15] D. Barnett, S. Block, G.J. Piermarini, *Rev. Sci. Instrum.* 44 (1973) 1.
- [16] S.A. Solin, A.K. Ramdas, *Phys. Rev. B* 1 (1970) 1687.
- [17] G.J. Piermarini, S. Block, J.D. Barnett, *J. Appl. Phys.* 44 (1973) 5377.
- [18] M.C. Martin, X. Du, J. Kwon, L. Mihaly, *Phys. Rev. B* 50 (1994) 173.