COMMUNICATIONS: SIF Congress 2010

A Raman scattering study of permanently densified vitreous B_2O_3

G. CARINI jr.

IPCF del C.N.R., Sezione di Messina - V.le F. Stagno d'Alcontres 37, I-98166 Messina, Italy
Dipartimento di Fisica, Università di Messina - V.le F. Stagno d'Alcontres 31, I-98166 Messina
Italy

Summary. — Inelastic light scattering spectra of normal and permanently densified B_2O_3 glasses were investigated over the frequency range between 6 and $1600\,cm^{-1}$. Densification from $1825\,kg/m^3$ up to $2082\,kg/m^3$ was obtained by loading B_2O_3 glasses in a multi-anvil apparatus for the synthesis at $2\,GPa$; they were fused at $1500\,K$ and then quenched at that pressure. The low-frequency Raman scattering includes the Boson peak, which dominates the spectra between 10 and $100\,cm^{-1}$. Densification significantly decreases the intensity of the Boson peak and shifts its position from about $26\,cm^{-1}$ up to $39\,cm^{-1}$. At higher frequencies, the spectral features of the bands associated to the vibrational motion of boroxol rings and BO_3 units building up the network indicate that these molecular groups keep the main characteristics of their conformation, even if the connectivity of these groups is varied as a consequence of a decrease of the ring concentration. These observations imply that densification drives the system toward a structure having a more efficient packing of molecular units.

PACS 78.30.Ly – Disordered solids.
PACS 63.50.Lm – Glasses and amorphous solids.

1. – Introduction

The vibrational dynamics at highest frequencies ($> 100\,GHz$) in glasses continues to be a very interesting and widely studied topic. In fact, the topological disorder in glassy structures leads to an excess density of low-energy vibrational states $g(\nu)$ over the Debye contribution, which gives a broad hump in the inelastic neutron and light scattering spectra, known as the "Boson peak" (BP) and frequently ascribed to structural correlations over the intermediate-range length scale [1-3]. In spite of numerous experimental and theoretical studies, the BP as well as other low-frequency anomalies of vibrational properties of glasses associated with low-energy excitations are not yet understood [4-6].

Recently, it has been shown that the Boson Peak arises mainly from transverse vibrational modes associated with defective soft structures of nanometer sizes in the glass [7].

This suggestion opens new ways for the investigation of the BP by applying "hot" densification of a glass, that is by quenching the melt of a glass-forming liquid subjected to high pressures (GPa range). Since the structure of "hot" densified glasses reflects the one of the supercooled liquid at high pressure at the glass transition temperature T_g, remarkable and controlled modifications of the short- and intermediate-range order without altering the stoichiometry of the system are expected.

An archetype of glassy oxides, such as B_2O_3, permanently hot densified at increasing pressures gave evidence of polymorphism (or better, polyamorphism) [8, 9], that is a transition from low- to high-density amorphous phases characterized by a coordination increase from 3 to 4 of network forming ions (NFI) and by significant variations of the intermediate-range order. Moreover, very recent studies based upon NMR measurements [9] revealed that the fraction of boroxol rings in hot densified glassy B_2O_3 decreases from a fraction of about 0.8 in the normal glass to about 0.3 in glasses compacted at increasingly higher pressure in the range between 2 GPa and 5.8 GPa. Boroxol rings (B_3O_6) are the molecular groups formed by connected BO_3 planar triangles which are the basic units building up the network of normal vitreous B_2O_3 [10-13]. The decrease of boroxol rings observed in compacted glasses should be related to the decrease of ring concentration with increasing temperature above T_g [14].

The present paper reports a study of the low- and high-frequency Raman scattering having as objective the analysis of the evolution of the Boson Peak and the modifications of the short- and medium-range order, which are induced by hot densification at 2 GPa of B_2O_3 glasses. In particular, the structural changes have been evaluated by a compared analysis of the boroxol breathing mode at $808 \, cm^{-1}$ and the high frequency multi-component band between 1200 and $1600 \, cm^{-1}$ associated with vibrations involving both boroxol rings and the residual network of BO_3 units.

2. – Experimental details

B_2O_3 glasses were prepared by melt-quenching using, as starting material, laboratory reagent 99.999% purity grades of boron oxide isotopically enriched in ^{11}B (99%), because the same samples considered for the present analysis will be used for future experiments of elastic and inelastic neutron scattering measurements. $^{11}B_2{}^{16}O_3$ powder was heated at $150 \,°C$ for 24 h in N_2 atmosphere in order to reduce any water content. The dehydrated powder was melted in an alumina crucible and a clear bubble free melt was obtained after 2 h at $1250 \,°C$. The melt was cast into a preheated $250 \,°C$ split steel mould to prepare a glass cylinder about 15 mm long and 6 mm in diameter. The glasses were annealed and stabilized at $\sim 540 \, K$ ($\sim 20 \, K$ above their calorimetric glass transition temperature T_g) in a high-purity nitrogen atmosphere and then cooled and stored at room temperature. Densification was obtained by loading B_2O_3 glasses in a multi-anvil high-temperature/high-pressure (HT/HP) apparatus for the synthesis at 2 GPa. They were fused under pressure at $1150 \,°C$ for about 10 (2 GPa-I) or 20 min (2 GPa-II) and then quenched at that pressure. A typical raw sample had a diameter and a length of 5 mm. Both the normal and compacted samples were clear, transparent, and good optical quality glasses. After the synthesis and also few months later, the densified B_2O_3 glasses were characterized by X-ray diffraction which did not reveal any sign of crystallization.

The density was measured at room temperature by a Micrometrics Accupyc 1300 gas pycnometer under helium gas having an accuracy of 0.03%. The densities of normal and densified B_2O_3 glasses are $1825 \, kg/m^3$ and $2082 \, kg/m^3$, respectively.
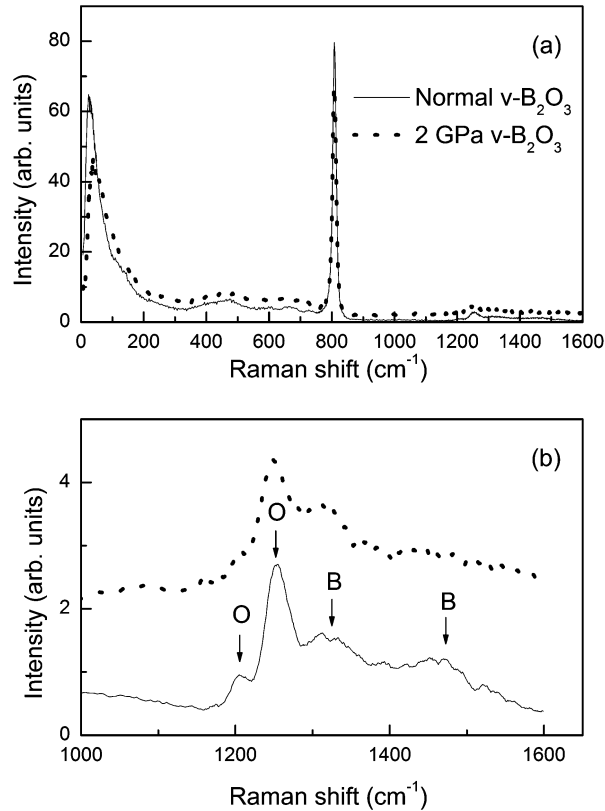
Fig. 1. – (a) Room temperature Raman spectra of normal and permanently densified ($2\,GPa$-I) B_2O_3 glasses for VV polarization; (b) high-frequency region of the spectrum.

The Raman spectra were performed at room temperature on a double monocromator Jobin-Yvon U-1000 and were recorded in 90° scattering geometry in both VV (incident and scattered light is polarized vertical to the scattering plane) and VH geometry (perpendicular polarizations). The incident light was the $514.5\,nm$ line of argon-ion laser with power kept below $300\,mW$, along with a polarization scrambler between the sample and the entrance slit of the spectrometer. The accuracy of all stated measurements is within $1\,cm^{-1}$. To minimize the effect of surface depolarization, the sample surfaces have been polished before each run of measurement.

3. – Results and discussion

In order to discuss the variations of the vibrational dynamics of v-B_2O_3 due to the densification, a preliminary short description of the vibrational spectrum characterizing the normal glass, which has been extensively studied by Raman spectroscopy [14-17] and molecular dynamics simulation [18], is in order. The Raman spectrum of v-B_2O_3 between 6 and $1600\,cm^{-1}$ is shown in fig. 1a for VV (polarized) configuration. It can be divided into two frequency regions: i) the low-frequency part (below $100\,cm^{-1}$) characterized by the boson peak at about $26\,cm^{-1}$ and ii) the high-frequency part which is

dominated by the very intense and highly polarized band at $808\,\mathrm{cm}^{-1}$, associated to a localized breathing-type vibration of oxygen atoms inside the plane boroxol ring composed by three corner sharing BO_3 [15-17]. The Raman scattering was also measured in VH (depolarized) configuration: the depolarization ratio and the spectral characteristics (frequency and full width at half height (FWHH)) are in close agreement with those reported by Windisch and Risen for a glass of $^{11}B_2^{16}O_3$ [16]. Further vibrational features characterizing the high frequency region are:

i) The lines below $750\,\mathrm{cm}^{-1}$ which reflect an optical-like motion of atoms inside the basic units building up the network [16, 17].

ii) The multi-component band between 1200 and $1600\,\mathrm{cm}^{-1}$, (fig. 1b, solid line), which is assigned a) to vibrations of oxygen atoms bridging two boroxol rings ($1202\,\mathrm{cm}^{-1}$) or a boroxol ring to the network of BO_3 units ($1253\,\mathrm{cm}^{-1}$) and b) to the boron motion in chainlike segments ($1323\,\mathrm{cm}^{-1}$) or in the residual network ($1457\,\mathrm{cm}^{-1}$) of connected BO_3 units [14-16]. Differently from the band at $808\,\mathrm{cm}^{-1}$ whose intensity strongly decreases with increasing temperatures above T_g, the line at $1323\,\mathrm{cm}^{-1}$ exhibits an increasing intensity while the one at $1457\,\mathrm{cm}^{-1}$ remains at most constant [14]. These observations led to conclude that the opening of boroxol rings with increasing temperature gives rise to the formation of chainlike segments of connected BO_3 units, leaving unaltered the concentration of the groups forming the residual network.

In the following we will focus on the behaviors of the mode at $808\,\mathrm{cm}^{-1}$, which reflects the ring population, and of the multi-component band, which arises from the whole network of triangular groups. The comparison between the integrated intensities of these spectral features gives us the possibility to evaluate possible changes of boroxol ring fraction with densification.

Figure 1a reports also the experimental Raman spectrum over the same frequency range for permanently densified glassy B_2O_3 ($2\,\mathrm{GPa}$-I). From fig. 1a and the comparison between the multi-component bands shown in fig. 1b, it appears that densification gives rise to significant changes in the low frequency region, leaving at most unaltered the high frequency part: i) the BP shows a relevant decrease of the intensity and shifts from 26 up to $39\,\mathrm{cm}^{-1}$; ii) the band at $808\,\mathrm{cm}^{-1}$ and the four components of the multi-component band between 1200 and $1600\,\mathrm{cm}^{-1}$ keep their positions, exhibiting a slight decrease of the intensity over a flat background due to a small contribution from fluorescence. The vibrational motion associated to boroxol rings and BO_3 units appears to be little affected by densification, leading to the conclusion that these molecular groups preserve the main characteristics of their conformation. In the light of the close similarity between the high-frequency spectra, it results that the application of pressure up to $2\,\mathrm{GPa}$ in the liquid phase seems to have the simple effect to hinder the variations of the network connectivity associated to the structural changes driven by increasing temperature above T_g. Pressure only limits the opening of boroxol rings without any apparent modification of the chemical bonding, at least for what concerns the vibrational features characterizing the high-frequency Raman scattering at room temperature. It is inferred that the formation of boroxol rings during the cooling process, always under pressure, is regulated by transformation of chainlike segments of BO_3, such as in normal v-B_2O_3 at atmospheric pressure. The only difference is that the quenching process drives the system towards a structure having a more efficient packing of the molecular units, in order to fit to the less volume available to it. Following this scheme of glass formation,
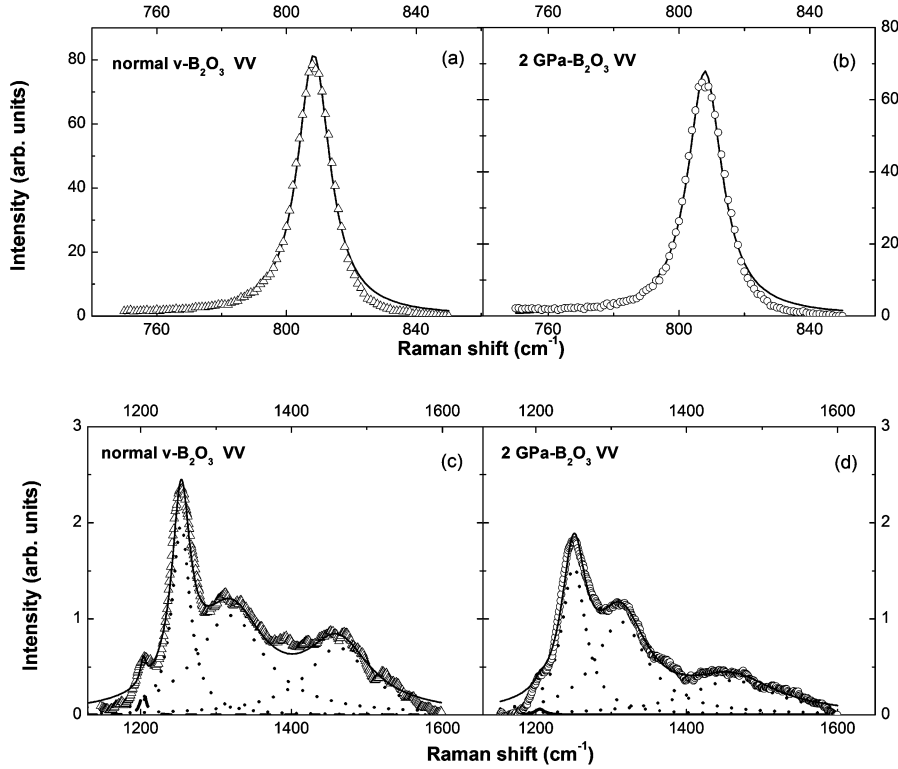
Fig. 2. – Room temperature Raman spectra in VV polarization of the $808\,\mathrm{cm}^{-1}$ mode (a, b) and the multi-component band between 1100 and $1600\,\mathrm{cm}^{-1}$ (c, d) of normal (Δ) and permanently densified (O) B_2O_3 glasses. Dashed and solid lines show the single Lorentzian fits and their addition, respectively.

it is expected that the line at $1457\,\mathrm{cm}^{-1}$ ascribed to BO_3 units building up the residual network should be temperature and also pressure independent, allowing us to use it as a reference for evaluating the variation of the boroxol ring fraction with densification. We will apply the following procedure which has been previously proposed for determining the changes of high-frequency modes in B_2O_3 glasses with different thermal histories [19]. First, it has been subtracted to each spectrum a background corresponding to the value of the scattered intensity in the high-frequency region, where no molecular vibrations are revealed. Afterwards, for each sample, the integrated intensities of the $808\,\mathrm{cm}^{-1}$ mode, associated to breathing mode of boroxol rings, and of the different lines forming the multi-component high-frequency band between 1200 and $1600\,\mathrm{cm}^{-1}$ have been evaluated by a Lorentzian fit. In particular, a multi-component fit has been used to decompose the latter band in four separate peaks, whose spectral characteristics for both the normal and compacted glasses are in agreement with the results of a previous analysis performed in a glass of $^{11}B_2{}^{16}O_3$ [16]. The results of the fits are shown in fig. 2 and the following values for the ratio, $R = I_{808}/I_{1457}$, between the intensities of the bands related to the fraction of boroxol rings (I_{808}) and the concentration of BO_3 units (I_{1457}) building up the residual disordered network are obtained: $R = 14.2$ for normal v-B_2O_3, $R = 14.1$
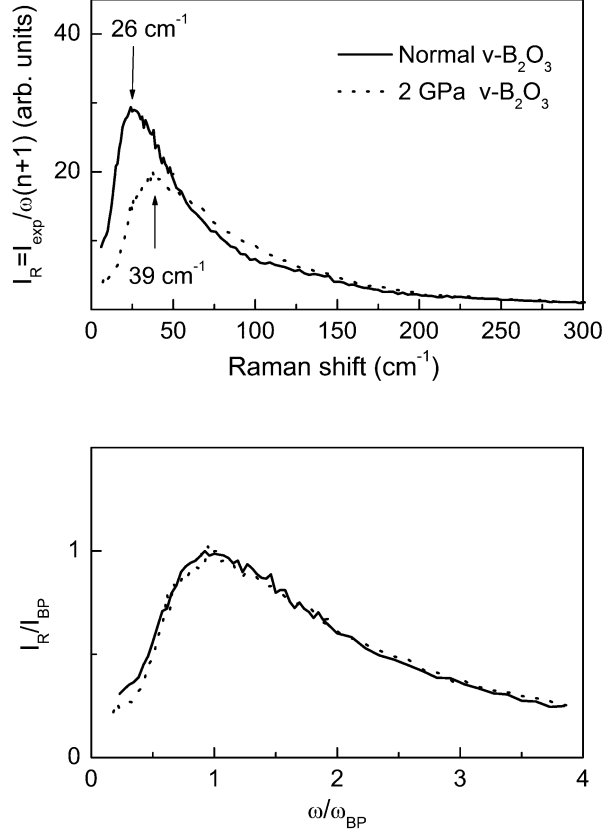
Fig. 3. – (a) Reduced Raman intensity I_R of normal and densified B_2O_3 glasses. (b) Comparison of the BP of normal (solid line) and densified (dotted line) B_2O_3 glasses, plotted as I_R/I_{BP} *vs.* ω/ω_{BP}.

for 2 GPa-I glass and $R = 12.8$ for 2 GPa-II glass. Taken together, these values point to a decrease of the fraction of boroxol rings with densification (about 10% in 2 GPa-II glass). In addition to this, we emphasize that no sign of the band at $770\,\mathrm{cm}^{-1}$ ascribed to vibrations of BO_4 groups [20] has been observed in both the compacted glasses, implying the lack of tetra-coordinated boron atoms associated to changes in chemical bonding.

These findings are in close agreement with very recent NMR results by Brazhkin *et al.* [9]. By analyzing B_2O_3 glasses compacted at different pressures up to 5.8 GPa, they revealed i) a decrease of the number of boroxol rings with increasing pressure and ii) the formation of tetra-coordinated boron atoms only for applied pressures higher than 5 GPa.

The low-frequency Raman spectra $(6–400\,\mathrm{cm}^{-1})$ of normal and densified v-B_2O_3 exhibit the same shape over the region between 300 and $400\,\mathrm{cm}^{-1}$ (see fig. 1), giving the possibility to use this part of the spectrum to normalize the data. The normalized and reduced Raman spectra of the two glasses at room temperature are shown in fig. 3a. It results that densification gives rise to a relevant increase of the BP frequency ω_{BP}, from 26 to $39\,\mathrm{cm}^{-1}$, while decreasing significantly its intensity. The reduced Raman intensity

I_R is proportional to the reduced density of low-energy vibrational states $g(\omega)/\omega^2$:

$$(1) \qquad I_R(\omega) = \frac{I_{exp}}{\omega\left[n(\omega, T) + 1\right]} = C(\omega)\frac{g(\omega)}{\omega^2}.$$

It has been proved, in fact, that the absence of translation symmetry gives rise to a low-frequency Raman intensity I_{exp} for a Stokes process, which reflects the product between the light-vibration coupling coefficient $C(\omega)$ and $g(\omega)$, accounting also for the Bose-Einstein population factor $n(\omega) = [e^{\frac{\hbar\omega}{k_b T}} - 1]^{-1}$ and the harmonic propagator $1/\omega$ [21]. The complexity of the vibrational characteristics of disordered systems affects both the functions $C(\omega)$ and $g(\omega)$, which exhibit, respectively, a linear frequency dependence and a behavior exceeding the Debye prediction over the frequency region of BP [22, 23].

An interesting result is given by plotting the curves of I_R scaled by the maximum intensity I_{BP} of the BP *vs.* the ratio ω/ω_{BP}, fig. 3b: despite the significant variations observed in the amplitude and the position of the BP with increasing density, both the scaled curves overlap showing an nearly identical shape. The small difference in the low-frequency tail of the peak is due to the different contribution of a further scattering process, the quasi-elastic light scattering excess (LSE) observed in glasses at frequencies below about 10–15 cm^{-1}. It is strongly temperature dependent and due to the coupling between the light and thermally activated fast relaxations [24]. Since very recent measurements of ultrasonic attenuation and velocity over the wide range from 1 K up to room temperature revealed that densification reduces significantly the local mobility of relaxors [25], a decrease of the relaxation strength regulating the LSE is expected by going from normal to compacted v-B_2O_3. The invariance of the shape leads to conclude that the product between $g(\omega)$ and $C(\omega)$ is independent of density and, most importantly, discloses the possibility for the existence of a low-energy vibrational dynamics underlying the BP where all the vibrational modes, extended and quasi-localized, are hybridized and form a distribution which does not change with densification.

4. – Conclusions

Raman light scattering measurements at room temperature over the frequency range between 6 and 1600 cm^{-1} in normal and permanently hot densified (at 2 GPa) v-B_2O_3 reveal that densification affects the connectivity and the intermediate range order of the glassy network. Analysis of the high-frequency Raman spectra shows that the main spectral characteristics of the vibrational bands characterizing the glassy network are preserved with increasing density, also disclosing a variation of the intensities which implies a decrease of the fraction of boroxol rings (B_3O_6) formed by connected BO_3 planar triangles. This finding leads to conclude that densification under pressure up to 2 GPa drives the system towards a structure having less free volume and a more efficient packing of the molecular units, in order to fit to the less volume available to it. Low-frequency Raman scattering below 150 cm^{-1} evidences that the BP decreases significantly in magnitude and increases in frequency from 26 cm^{-1} up to 39 cm^{-1} with increasing density. Despite these variations, all the scaled curves overlap showing an identical shape. The invariance of the shape leads to conclude that all the vibrational modes, extended and quasi-localized, contributing to the BP form a distribution which appears to be independent of density.

REFERENCES

[1] BUCHENAU U., ZHOU H. M., NÜCKER N., GILROY K. S. and PHILLIPS W. A., *Phys. Rev. Lett.*, **60** (1988) 1318.
[2] SOKOLOV A. P., BUCHENAU U., STEFFEN W., FRICK B. and WISCHENEWSKI A., *Phys. Rev. B*, **52** (1995) R9815.
[3] FONTANA A., ROSSI F., CARINI G., D'ANGELO G., TRIPODO G. and BARTOLOTTA A., *Phys. Rev Lett.*, **78** (1997) 1078.
[4] RUFFLÈ B., PARSHIN D. A., COURTENS E. and VACHER R., *Phys. Rev. Lett.*, **100** (2008) 015501.
[5] NISS K. *et al.*, *Phys. Rev. Lett.*, **99** (2007) 055502.
[6] MONACO G. and GIORDANO V. M., *Proc. Natl. Acad. Sci. U.S.A.*, **106** (2009) 3650.
[7] D'ANGELO G., CARINI G., CRUPI C., KOZA M., TRIPODO G. and VASI C., *Phys. Rev. B*, **79** (2009) 014206.
[8] BRAZHKIN V. V. and . LYAPIN A. G., *J. Phys. Condens. Matter*, **15** (2003) 6059.
[9] BRAZHKIN V. V., FARNAN I., FUNAKOSHI K., KANZAKI M., KATAYAMA Y., LYAPIN A. G. and SAITOH H., *Phys. Rev. Lett.*, **105** (2010) 115701.
[10] BRAY P. J., *J. Non-Cryst. Solids*, **73** (1985) 19.
[11] JOO C., WERNER-ZWANZIGER U. and ZWANZIGER J. W., *J. Non-Cryst. Solids*, **261** (2000) 282.
[12] YOUNGMAN R. E., HAUBRICH S. T., ZWANZIGER J. W. *et al.*, *Science*, **269** (1995) 1416.
[13] SWENSON J. and BORJESSON L., *Phys Rev B*, **55** (1997) 11138.
[14] HASSAN A. K., TORREL L. M., BORJESSON L. and DOWEIDAR H., *Phys. Rev. B*, **45** (1992) 12797.
[15] GALEENER F. L., LUCOVSKY G. and MIKKELSEN J. C. jr., *Phys. Rev. B*, **22** (1980) 3983.
[16] WINDISCH C. F. jr. and RISEN W. M. jr., *J. Non-Cryst. Solids*, **48** (1982) 307.
[17] BARRIO R. A., CASTILLO-ALVARADO F. L. and GALEENER F. L., *Phys. Rev. B*, **44** (1991) 7313.
[18] UMARI P. and PASQUARIELLO A., *Phys. Rev. Lett.*, **95** (2005) 137401.
[19] SUROVTSEV N. V., WIEDERSICH J., BATALOV A. E., NOVIKOV V. N., RAMOS M. A. and ROSSLER E., *J. Chem. Phys.*, **113** (2000) 5691.
[20] CARINI G., CUTRONI M., FONTANA A., MARIOTTO G. and ROCCA F., *Phys. Rev. B*, **29** (1984) 3567.
[21] SHUKER R. and GAMMON R. W., *Phys. Rev. Lett.*, **4** (1970) 222.
[22] SUROVTSEV N. V. and SOKOLOV A. P., *Phys. Rev. B*, **66** (2002) 054205.
[23] FONTANA A. *et al.*, *J. Phys. Condens. Matter*, **19** (2007) 205145.
[24] CARINI G., FEDERICO M., FONTANA A. and SAUNDERS G., *Phys. Rev. B*, **47** (1993) 3005.
[25] CARINI G. jr. and TRIPODO G., unpublished results.