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THE STRUCTURE OF HYDROGENATED AMORPHOUS SILICON-CARBON ALLOYS AS INVESTIGATED BY EXAFS

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ABSTRACT

We have studied the local structure of hydrogenated amorphous silicon-carbon alloy films, $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, by measuring the extended x-ray absorption fine-structure (EXAFS) at the Si K edge.

We find that first coordination shell average bond lengths are 2.35 Å for Si-Si and 1.86 Å for Si-C and are constant with concentration to within ± 0.015 Å.

By comparing the composition of the first coordination shell around Si with the average concentration we show that the alloy tends to be chemically ordered, in that heteroatomic bonds are preferred.

INTRODUCTION

Besides their technological importance, hydrogenated amorphous silicon carbon alloys, $a\text{-Si}_{1-x}\text{C}_x\text{:H}$, are interesting also from a fundamental point of view, in regard to understanding the effect of local silicon, carbon and hydrogen bonding configurations on the film properties. Moreover, the ability of carbon to have twofold, threefold, and fourfold coordination adds a degree of freedom in local structural arrangement which is absent in other amorphous semiconductor alloys. In this context, of special interest is the problem of chemical ordering i.e. the relative arrangement of silicon and carbon atoms on the sites of the amorphous network.

A variety of techniques have been employed to obtain information on the local structure in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ (see reference 1 and references therein). Results are consistent with a complex picture in which the macroscopically homogeneous films are microscopically heterogeneous and composed of different phases: an amorphous polymeric tissue (only C and H atoms),

amorphous graphitic clusters (only C atoms), an amorphous alloy component of Si, C and H atoms, and voids. An important issue for $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ is the nature of the bonding of the Si and C atoms in the amorphous alloy component.

There are very few direct structural studies of these films. A preliminary EXAFS study at the Si K edge^{2,3}, was performed in our group on alloys prepared by glow discharge decomposition. It was found that the average Si-Si bond length was equal to the crystalline value of 2.35 Å, while the Si-C bond length was slightly lower than the c-SiC value of 1.88 Å, with an average of 1.86 Å. An electron diffraction study⁴ showed that, under certain deposition conditions and for a nearly equiatomic composition, a completely chemically ordered structure was obtained; films prepared under other conditions with similar as well as different compositions were described as partially chemically ordered. Finally, an electron energy loss fine structure study⁵ on stoichiometric films, prepared by radio frequency reactive sputtering in argon atmosphere, indicated that in a-SiC, hydrogenated or not, each Si atom is surrounded by nearly four C atoms and viceversa.

In this work we report more detailed studies by EXAFS of first shell local structure (bond lengths and coordination numbers) on a series of glow discharge $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ samples. On one of the samples also second shell results are reported and discussed. The final aim of the present work is to try to answer the still open question as to whether there is a preference for heteroatomic bonding in the amorphous alloy component, as seen from the Si atom.

EXPERIMENT

The $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ samples were prepared by radio frequency (RF) glow-discharge decomposition of SiH_4 and CH_4 and were deposited at a substrate temperature of 200 °C. The RF power at 13.56 MHz was approximately 5 W. The gases were mixed to the desired ratio in a separate gas handling system and delivered at a constant flow rate of 20 sccm; the pressure during deposition was kept constant and equal to 0.2 Torr. The base vacuum was 10^{-7} Torr and high purity gases were used. Samples were deposited on Be foils for the EXAFS experiments.

The deposition rates, determined by the interference function of a laser beam reflected off the sample surface during growth, varied between 0.1 and 1 Å/s, increasing as the CH_4 percentage in the mixture decreased. Final film thicknesses were in the range 0.45 to 1.6 μm. Four different alloy compositions were investigated as well as pure a-Si:H.

Samples were transferred in UHV (10^{-9} Torr) to an analysis chamber (10^{-11} Torr) where Auger measurements were performed to obtain average concentration values, using a Perkin Elmer electron gun and double pass cylindrical mirror analyzer system. No signal relative to the presence of oxygen was observed in any of the samples or of carbon contamination on the a-Si:H sample's surface. The compositions of the five samples are listed in Table I.

X-ray absorption measurements at the Si K-edge were performed at the PULS synchrotron radiation facility of the Laboratori Nazionali di Frascati. The storage ring was operated at 1.5 GeV and the average current was approximately 40 mA. The x-ray radiation was monochromatized using a InSb(111) double crystal monochromator. The crystals were slightly detuned to eliminate harmonics from the output beam. Data were collected in the transmission mode by simultaneously recording the current from two ion chambers with nitrogen fill gas, one placed upstream and the other downstream from the sample. The energy calibration was set as 3206 eV at the argon K edge. Samples were held in vacuum (10^{-5} Torr) and were composed of several layers of film on Be foil so that the total thickness, chosen to optimize the signal to noise ratio, varied between 2 μm and 4 μm.

TABLE I - Columns 2 and 3 contain the values of x and x' as explained in the text. Columns 4 -12 contain the values of the structural parameters obtained from the best fits of the filtered EXAFS signal. $N_{\text{Si-C}}$, $N_{\text{Si-Si}}$, and $N_{\text{Si-C-Si}}$ are the coordination numbers and $\Delta\sigma^2_{\text{Si-C}}$, $\Delta\sigma^2_{\text{Si-Si}}$, and $\Delta\sigma^2_{\text{Si-C-Si}}$ are the disorder factors, both relative to the model compounds.

No	x	x'	$N_{\text{Si-C}}$	$R_{\text{Si-C}}$ (Å)	$\Delta\sigma^2_{\text{Si-C}}$ (10^{-3}Å^2)	$N_{\text{Si-Si}}$	$R_{\text{Si-Si}}$ (10^{-3}Å^2)	$\Delta\sigma^2_{\text{Si-C}}$ (Å)	$N_{\text{Si-C-Si}}$ (10^{-3}Å^2)	$R_{\text{Si-C-Si}}$	$\Delta\sigma^2_{\text{Si-C-Si}}$
1	0.00	0.00	0.00			1.00	2.35	0.0			
2	0.26	0.26	0.17	1.85	-3.1	0.79	2.35	-0.6			
3	0.44	0.38	0.41	1.84	2.2	0.28	2.34	-1.0	0.15	3.11	4.6
4	0.57	0.40	0.63	1.87	3.1	0.23	2.36	6.3			
5	0.86	0.65	1.00	1.87	0.0	0.00					

RESULTS

The Si K-edge absorption spectra were analyzed according to standard procedures⁶ in the energy interval 1800 eV to 2250 eV. The pre-edge region was fitted with a linear function while the absorption above the edge with a smooth curve formed by three cubic splines to simulate the atomic cross section. The value of E_0 was chosen as the maximum of the derivative of the absorption edge. Raw EXAFS oscillations obtained are reported in the left panel of Fig. 1.

Two complementary data analyses were used. The Fourier transform technique provided a qualitative picture of local coordination around Si, while a quantitative determination of the structural parameters was obtained by a thorough analysis in k space.

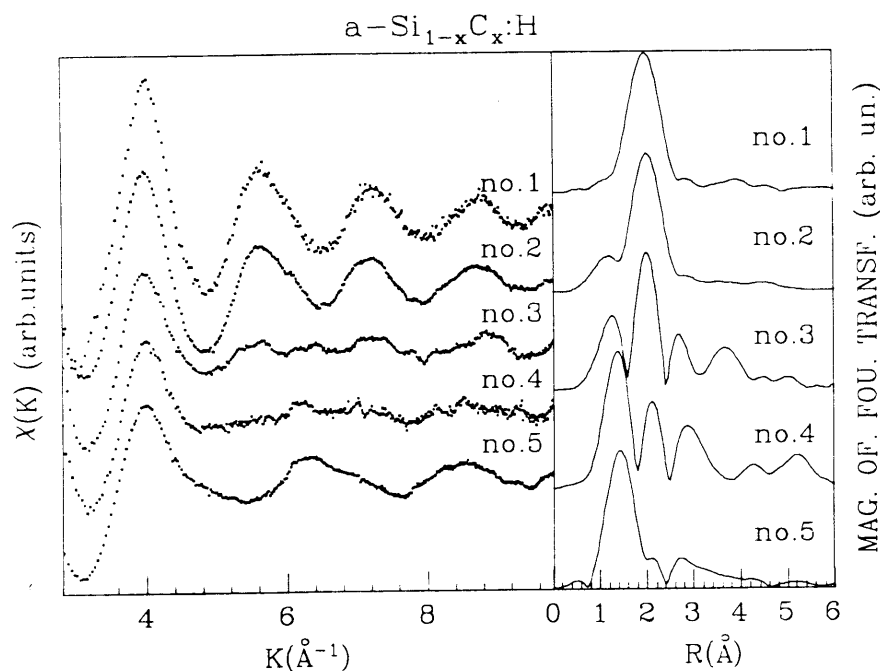


FIG 1 - In the left hand panel we show the raw EXAFS data. Magnitude of the Fourier transforms are shown on the right.

A. Fourier transform analysis

The raw EXAFS spectra multiplied by k were Fourier transformed using a gaussian window in a k range of 2.5 - 10.0 \AA^{-1} . The Fourier transforms (FT) obtained with this procedure are shown on the right panel of Fig. 1 (no phase shift correction has been applied).

The FT relative to sample no.1 (a-Si:H) shows a single peak at an apparent distance $R = 1.99 \text{\AA}$ which is equal to the value obtained by analyzing, with the same procedure, a crystalline sample of Si (c-Si). This peak corresponds to the Si-Si bond distance at 2.35 \AA (once the phase shift is taken into account) and is consistent with previous measurements^{7,8} which indicate that a-Si:H and c-Si have identical average bond length.

Also the FT of sample no.5 ($x = 0.86$) shows a single peak, at $R = 1.45 \text{\AA}$. We have compared this FT with the spectrum obtained on tetramethyl silane gas, $\text{Si}(\text{CH}_3)_4$. In this molecule a central Si atom is surrounded by four methyl groups, with a Si-C bond distance of 1.87 \AA .⁹ The FT of the $\text{Si}(\text{CH}_3)_4$ spectrum also shows a single peak at the same value of R . By assuming phase transferability we conclude that the Si-C interatomic distance in sample no.5 is equal to 1.87 \AA , which compares well with the c-SiC value of 1.88 \AA .

The FT's relative to the alloys with intermediate composition can be viewed, in the range $0.0 \leq R \leq 2.4 \text{\AA}$, as a combination of the two configurations corresponding to the Si-Si and Si-C bonds. Starting from sample no.1 we notice how the Si-Si peak gradually disappears as the Si-C peak rises.

Signals relative to higher coordination shells ($R > 2.4 \text{\AA}$) are present in the FT's of samples no.3 and no.4. Possible second shell configurations are Si-C-C, Si-C-Si, Si-Si-C, and Si-Si-Si, where the first symbol is the central Si atom and the second and third symbols refer to the atoms in the first and second coordination shell respectively. We shall perform a second shell analysis on sample no.3 and test for the presence of each of these contributions.

B. k space analysis

Quantitative data analysis was performed in k space. An inverse Fourier transform of the R space data was performed in order to "filter out" unwanted higher shell contributions and noise. The Fourier filtered data was then compared to model EXAFS spectra. The amplitudes and phases of the Si-Si and Si-C pairs for these model spectra were obtained from the experimental data of model compounds in which bonding configurations similar to those being investigated are present. These functions were then used to build EXAFS spectra relative to the two atomic pairs using the standard EXAFS formula but leaving coordination numbers $N_{\text{Si-Si}}$ and $N_{\text{Si-C}}$, interatomic distances $R_{\text{Si-Si}}$ and $R_{\text{Si-C}}$ and mean square relative displacements $\Delta\sigma^2_{\text{Si-Si}}$ and $\Delta\sigma^2_{\text{Si-C}}$ as fitting parameters. A linear combination of these two signals was then used as a model in a least squares fitting routine until a best fit was obtained. If a third contribution was added, e.g. a Si-Si pair in a Si-C-Si configuration, a third signal was added to the linear combination, as well as three more fitting parameters: $N_{\text{Si-C-Si}}$, $R_{\text{Si-C-Si}}$, $\Delta\sigma^2_{\text{Si-C-Si}}$. As for the values of E_0 we checked that small variations ($\pm 2.5 \text{ eV}$) of this parameter leave the fits unaltered; therefore this parameter was not varied during the fits. The fitting procedure was performed in the range 2.8 to 9.8 \AA^{-1} .

The obvious choice for the models in our case are sample no.1 and sample no.5. In sample 1 (a-Si:H) local bonding parameters are very similar to those of c-Si^{7,8}: $R = 2.35 \text{\AA}$, $N = 3.7$ to 4 atoms and $\sigma^2 = 4$ to 4.5 $\cdot 10^{-3} \text{\AA}^2$. In this sense sample 1 is a very well characterized model. As for sample 5 as explained above the FT analysis shows a single Si-C peak at 1.87 \AA . This is consistent with the high C concentration (especially if there is a high

chemical order). The coordination number of Si in this case is expected to be close to 4, within 10%, as no change in valence should occur and there is limited bonding of H to Si.

A first shell analysis has been performed on all samples; for this the inverse Fourier transform was performed in the R range 1.0 - 2.4 Å. A second shell analysis was performed on sample no.3 and the R space window was extended to 3.3 Å. We tested for the various bonding configurations described above and an acceptable fit was obtained only for a Si-C-Si second shell contribution.

The best fitting parameters obtained are reported in Table I. In Fig. 2 we show the comparison between the fits and the Fourier filtered data. When comparing the coordination numbers listed in table 1 with the intuitive picture given by the FT's of fig. 1 it must be kept in mind that Si-C bonds give rise to weaker peaks in the FT with respect to Si-Si bonds, due to the smaller backscattering function of C. This explains that, for example, in sample 3 we obtain $N_{\text{Si-C}} > N_{\text{Si-Si}}$ while the peak due to the Si-C bonds is lower than that relative to Si-Si.

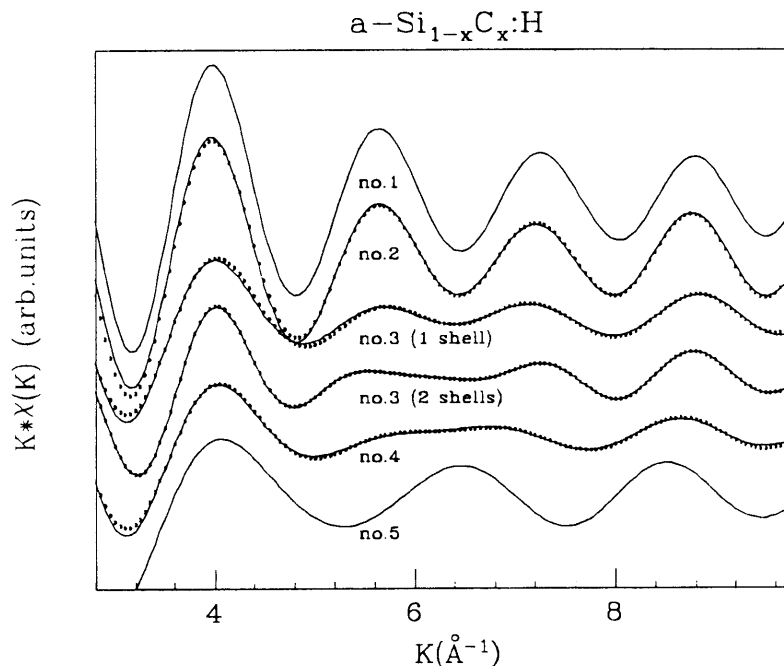


FIG. 2 - Best fits to the filtered EXAFS signal, obtained as explained in the text. We show the inverse Fourier transform as the solid line and fits as the dotted line.

DISCUSSION

From the values reported in table 1 we note that the first shell average bond lengths do not change with composition to within ± 0.015 Å. In particular, we can confirm the first shell interatomic distance values obtained in a preceding work on a comparative EXAFS study of different amorphous hydrogenated alloys², comprehensive of the a-Si_{1-x}C_x:H alloy. In Fig. 3 we report the average first shell interatomic distances for this alloy as a function of atomic concentration. Constancy in interatomic distances has already been observed in amorphous semiconductor alloys^{3,10,11} and it is attributed to the lack of long-range order which allows relaxation of the distances to their "molecular" value. As for second shell interatomic distances, the value of 3.11 Å obtained for the Si-Si pair in a Si-C-Si configuration compares well with the crystalline value of 3.08 Å for the same configuration in cubic SiC.

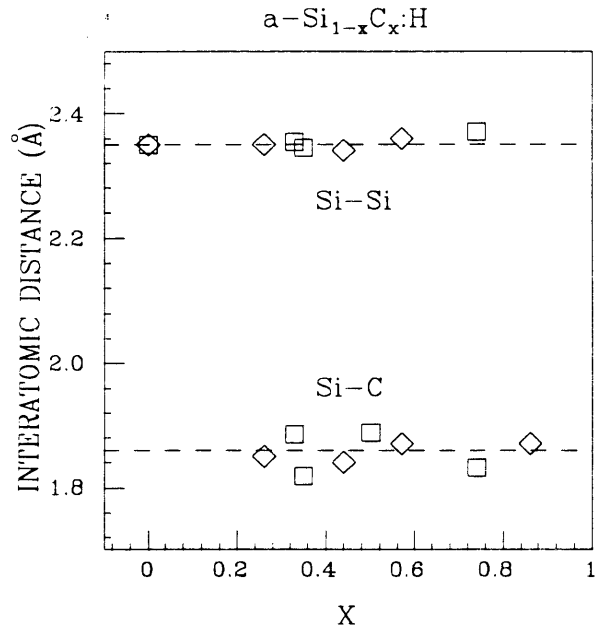


FIG. 3 - First shell interatomic distances in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ as a function of atomic concentration. Diamonds indicate present results and squares indicate previous results². The Si-Si distance is $2.35 \pm 0.01 \text{ \AA}$ and the Si-C distance is $1.86 \pm 0.015 \text{ \AA}$.

In order to check for the presence of chemical ordering in the alloy component of the material we compared experimental relative coordination numbers $N_{\text{Si-C}}/(N_{\text{Si-Si}}+N_{\text{Si-C}})$ with theoretical values obtained for the two extreme cases: a total chemical ordering or a random distribution of the two types of bonds. In the former case homonuclear bonds between minority type atoms are absent, while in the latter the distribution of atoms is purely statistical and all types of bonds are allowed with the same intrinsic probability. For a binary amorphous alloy with average carbon composition given by x' these values can be calculated¹² as a function of total coordinations N_{Si} ($N_{\text{Si}}=N_{\text{Si-Si}}+N_{\text{Si-C}}$) and N_{C} ($N_{\text{C}}=N_{\text{C-C}}+N_{\text{C-Si}}$) and average coordination $\langle N \rangle = (1-x')N_{\text{Si}} + x'N_{\text{C}}$. In our calculations we shall assume that $N_{\text{Si}} = 4$. In doing so we are committing a small error. In fact, N_{Si} is slightly smaller than four because of H bonding: since EXAFS is not sensitive to hydrogen this results in a reduction of the "effective" coordination. IR measurements¹³ show that the number of Si-H bonds varies with carbon content but is always quite small, i.e. lower than 10% of the total Si bonds. Therefore the "effective" Si coordination is within 10% equal to 4. On the other hand the number of C-H bonds is not negligible. IR spectra^{13,14,15} as well as mass density measurements¹⁶ on glow discharge $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ show that carbon is incorporated mainly as methyl groups and estimates for the C-H bond content are as high as 33%^{13,17} of the total C bonds. This would bring the "effective" coordination down to 2.7. Since it is impossible to determine the value of N_{C} from Si K edge results we shall compare our experimental relative coordination numbers around Si with the theoretical values calculated for N_{C} in the range 2 to 4.

In our case x' refers to the composition in the alloy component which is not equal to the mean total composition x and $x' < x$; this is due to the presence of amorphous polymeric tissue and amorphous graphitic clusters^{13,18} along with the silicon-carbon alloy phase. Electron energy loss spectroscopy studies¹⁹ on our alloys give evidence that both graphitic and polymeric components increase with carbon content. The low energy loss spectra give qualitative information on the presence of the different components in the material, since the presence of C-C bonds in sp^2 hybridization is directly signaled by the presence of a loss peak in the range 4 to 7 eV. A quantitative analysis is performed by comparing the Auger spectra with appropriate model compounds, allowing the fraction of segregated carbon atoms in the films to be estimated. While the details of this work are being published elsewhere¹⁹ in the present paper we use the values of x' obtained in this way. It is interesting to note that these values are in good agreement with those found by optical spectroscopy in reference 13.

The values of x' corresponding to the values of x are reported in Table I. In Fig. 4 we report the comparison between our experimental values of $N_{\text{Si-C}}/N_{\text{Si}}$ and theoretical values calculated for the two cases of a random distribution of bonds and of a totally chemically ordered structure, as a function of x' .

In the random case three experimental points lie outside the physically acceptable region of N_{C} . On the other hand the right hand panel clearly shows that there is a strong preference for heteroatomic bonding in all samples. A random distribution of bonds cannot however be excluded in the sample with low carbon content. This result confirms previous results on local order in amorphous semiconductor alloys. The same result was obtained for $\text{a-Si}_{1-x}\text{N}_x$ ^{2,3}. The tendency to local chemical order that these films display is not surprising keeping in mind that in the crystalline phase Si and C (or Si and N) are immiscible and form stoichiometric silicon carbide (or Si_3N_4). On the other hand, results on $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$ ^{3,10} show that there is a random distribution of bonds in the films, which agrees with the complete miscibility of the two elements already established in the crystalline alloys. Finally, the second shell signal detected in the spectra relative to samples no.3 and no.4 is evidence of a higher degree of local order at compositions around stoichiometry. The fact that we observe only Si-C-Si configurations is in qualitative agreement with the presence of a high degree of chemical order in the alloy phase.

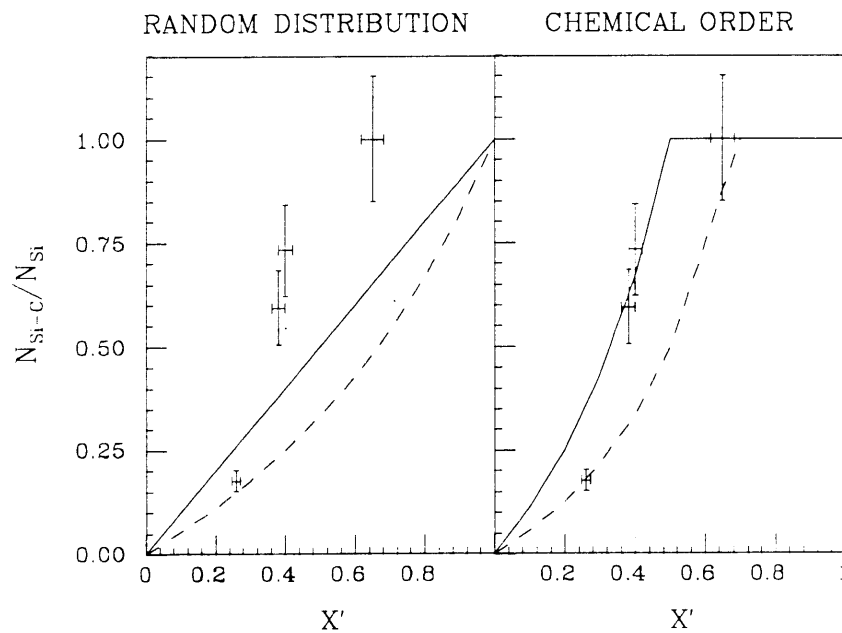


FIG 4 - Comparison of experimental relative coordination numbers with theoretical values obtained for the two cases of a random distribution of bonds (left panel) and a totally chemically ordered structure (right panel). Solid lines are calculated using $N_{\text{C}} = 4$, while dashed lines are for $N_{\text{C}} = 2$. Clearly the chemically ordered case fits the data best.

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REFERENCES

1. J. Bulloot and M. P. Schmidt, *Phys. Stat. Sol. (b)* 143, 345 (1987).
2. A. Filipponi, P. Fiorini, F. Evangelisti, and S. Mobilio, *MRS Symp. Proc.* 95,305 (1987).
3. S. Mobilio and A. Filipponi, *J. Non-Cryst. Solids* 97&98, 365 (1987).
4. D.R. McKenzie, G.B. Smith, and Z.Q. Liu, *Phys. Rev. B* 37, 8875 (1988).
5. A.E. Kaloyeros, R.B. Rizk, and J.B. Woodhouse, *Phys. Rev. B* 38, 13099 (1988).
6. P.A. Lee, P.H. Citrin, P. Eisenberger, and B.M. Kincaid, *Rev. Mod. Phys.* 53, 769 (1981).
7. A. Balerna, M. Benfatto, S. Mobilio, C.R. Natoli, A. Filipponi, and F. Evangelisti., *J. de Physique C8*, 63 (1986).
8. A. Filipponi, F. Evangelisti, M. Benfatto, S. Mobilio, and C.R. Natoli *Phys. Rev. B* 40, 9636 (1989).
9. B. Beagley, J.J. Monaghan, and T.G. Hewitt, *J. Mol. Struct.* 8, 401 (1971).
10. L.Incoccia, S. Mobilio, M.G. Proietti, P. Fiorini, C. Giovannella, and F. Evangelisti, *Phys. Rev. B* 31, 1028 (1985).
11. F. Boscherini, A. Filipponi, S. Pascarelli, F. Evangelisti, S. Mobilio, F.C. Marques, and I. Chambouleyron, *Phys. Rev. B* 39, 8364 (1989).
12. G.S. Cargill III and F. Spaepen, *J. Non-Cryst. Solids* 43, 91 (1981).
13. K. Mui, D.K. Basa, F.W. Smith, and R. Corderman, *Phys. Rev. B* 35, 8089 (1987).
14. F. Demichelis, G. Kaniadakis, E. Mezzetti, P. Mpawenayo, A. Tagliaferro, E. Tresso, P. Rava, and G. Della Mea, *Il Nuovo Cimento* 9 D, 393 (1987).
15. A.H. Mahan, B. von Roedern, D.L. Williamson, and A. Madan, *J. Appl. Phys.* 57, 2717 (1985).
16. J. Sotiropoulos and G. Weiser, *J. Non-Cryst. Solids* 97&98, 1087 (1987).
17. M.A. Petrich, K.K. Gleason, and J.A. Reimer, *Phys. Rev. B* 36, 9722 (1987).
18. G.B. Smith and D.R. McKenzie, *J. Appl. Phys.* 65, 1694 (1989); K. Mui and F.W. Smith, *Phys. Rev. B* 38, 10623 (1988).
19. M. De Seta, P. Narducci, and F. Evangelisti, unpublished.