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X-RAY ABSORPTION SPECTROSCOPY: THE THREE-BODY CORRELATION FUNCTION IN AMORPHOUS SILICON

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ABSTRACT

We present preliminary experimental results on the main peak of the three body distribution in a-Si and a-Si:H obtained using an ab-initio data analysis procedure. Multiple scattering is found to contribute significantly to the spectra. We have determined the physical parameters involving three-body correlations in a-Si and a-Si:H. The results are compared with recent computer simulations of continuous random network models. The a-Si:H material is found significantly more ordered in both bond and angle distributions.

The importance of a technique which allows to derive any kind of information beyond the radial distribution function ($g_2(r)$) is large in various fundamental or applied fields of research. In the following we shall discuss the experimental extraction of the relevant features of the three-body correlation function (g_3) in amorphous silicon (a-Si and a-Si:H) by means of the x-ray absorption spectroscopy (XAS).

Structural information on the a-Si (or similar materials) g_2 has been obtained in several x-ray and neutron diffraction experiments.[1-3] This information, however, is not able to characterize the structure completely. The knowledge of the g_3 parameters provides a more detailed information on the atomic arrangements and particularly on the bond angle distribution, whose determination from the g_2 is ambiguous, as well as on the bond-bond and bond-angle correlations.

The possibility to gain structural information beyond the g_2 by means of the XAS has recently driven much attention on the subject.[4] The presence of a multiple-scattering (MS) signal in the absorption spectra of several compounds is nowadays accepted by the majority of the scientific community. Despite of the generally weak intensity of the MS signal and of its limited extension in energy, with respect to single-scattering (SS), we show that it is possible to derive information on higher order structural correlation functions.

MS contributions in silicon systems have been identified both in c-Si [5] and a-Si [6]. In a-Si the MS intensity is found of about 10% of the EXAFS, well beyond the noise level. It turned out that, in the a-Si case, the experimental spectrum could be reproduced only if MS signals associated to the main peak of the g_3 were taken into account using an appropriate theory to calculate the exact configurational average.[7] The agreement between calculated signals and experiment was very good [6] suggesting the possibility to attempt a fitting of the unknown structural parameters of the g_3 peak.

In this contribution we present the results of this analysis performed on the XAS spectra of a-Si prepared by ion beam sputtering at room temperature and glow-discharge a-Si:H. The SS and MS paths that have to be included in the calculation for amorphous silicon materials originates from the first two peaks of the g_2 , and from the main peak of the g_3 . [8] This last feature is due to the basic triangular arrangement of the atoms in the tetrahedral coordination with two first-neighbor bonds and connected by the 109.47 degrees angle. The analysis of the experimental signal provides information on the shape of such peak which is defined by the average geometry and the higher moments of the distribution. In particular the covariance matrix is in this case unambiguously defined by the four parameters: σ^2_R , σ^2_θ , $\sigma^2_{R_1,R_2}$, $\sigma^2_{R,\theta}$ as indicated in a previous paper. [8] The first is also obtainable from the g_2 first shell peak, however, the bond angle variance, the bond-bond and bond-angle correlations provide a new information which can be compared with the models.

Computer modeling of the amorphous structure has historically given a deep insight into the problem. Recently the application of Monte Carlo-like [9] or molecular dynamics techniques [10] has brought a renewed interest into this matter.

The experimental Si K-edge x-ray absorption spectra show, [7] besides the trivial first shell SS signal at $R \approx 2.0 \text{ \AA}$, a high frequency contribution in the region $3.5 < R < 4.5 \text{ \AA}$. The 4.5 \AA limit puts a serious bound to the length of the MS paths and therefore to the g_2 and g_3 features which may contribute to the spectrum. This excludes both paths involving distant neighbors and paths of higher order in the scattering which are ruled out by structural disorder. As shown in Ref. 6 the paths contributing to the high frequency signal are: (a) the χ_2 of the second shell of the g_2 , (b) the degenerate χ_4 due to the first shell of the g_2 , and (c) two χ_3 and three χ_4 associated to the peak (1) of the g_3 . The MS contributions depending on the same feature of a g_n are not independent and only their sum has a meaning.

The fitting of the experimental absorption spectra has been performed using a model signal formed by a polynomial background, a discontinuity to take into account of the KL-edge, [11] and a theoretical SS+MS signal built using fixed theoretical phases and amplitudes and adjustable structural parameters. The advantages in fitting directly the absorption are that the arbitrariness in the background extraction, especially in the near-edge region is overcome. The fitting program follows a previously used scheme, [11,7] the innovative aspect is that for the first time ab-initio theoretical phase-shifts are used instead of experimental ones.

In Fig. 1 we report the total model signals, composed of all the partial MS contributions due to the main peak of the g_3 , compared with the experimental residuals of a-Si and a-Si:H. The experimental high-frequency residuals are very different reflecting the structural differences of the two films. The good agreement of the model signals with the residuals indicates the quality of the fitting. We note also that the error is not entirely due to the experimental noise, indicating the presence of a higher frequency contribution ($5 < R < 6 \text{ \AA}$) in the near-edge region. This very small signal does not affect the structural results obtained on the g_3 main peak and we identified it as due to the third-neighbor distribution.

In Tab. 1 we report the experimental covariance matrix for the g_3 main peak as determined from the fitting for the a-Si and a-Si:H spectra, compared with the structural contributions in the WWW, [9] and BGS [10] models. The thermal contribution provides a relevant correction only on the first-neighbor distance variance which in the gaussian approximation is just summed to the structural one.

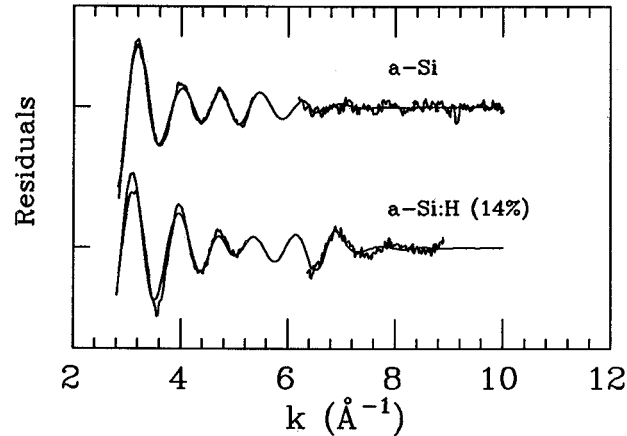


Figure 1: Comparison between the experimental residuals and the total theoretical residual contributions. The offset among the spectra is 0.04 units.

	$\sigma_R^2 (10^{-3} \text{ \AA}^2)$	$\sigma_\theta (\text{deg})$	$\rho_{R,\theta}$
WWW Model	3.6	11.3	0.145
BGS Model	2.3	15.1	0.048
a-Si	5.7(1)	9.6(2)	0.15(5)
a-Si:H	4.5(1)	8.9(2)	0.07(5)

Table 1: Parameters of the main peak of the three-body correlation function in a-Si and a-Si:H derived from the experiment and in the WWW and BGS models (structural contribution).

It has been shown [12] that the a-Si thermal contribution is practically equal to the c-Si value $\sigma_R^2=3.4 \times 10^{-3} \text{ \AA}^2$ at 300 K.

The error reported are statistical with 95% of confidence level. The correlation among the four structural parameters is small as we have verified. Systematic errors introduced by allowed variations of the parameters of the theory (MFP, threshold energy, ...) are found not relevant. On the contrary the $g_3(1)$ covariance matrix determines the relative weight of the second shell SS and various MS signals.

It clearly appears that in the a-Si case our experimental values of the bond length and angle variances are smaller than those obtained in either models. Provided the thermal contribution is taken into account, our bond length variance is in very good agreement with the BGS model, which on the other hand has a very broad bond angle distribution. The WWW model gives both values slightly larger than our experimental determination. The remarkable reduction of the bond and angle variances in the case of a-Si:H indicates an increase of the level of order both in the first and in the second coordination shell.

The values for the bond-angle and bond-bond correlations $\rho_{R\theta}$ are here determined for the first time. They present interesting consequences. We found the bond and adjacent angle fluctuation slightly correlated. The experimental value is found in agreement with the WWW model, while the smaller value reported in the BGS model lies out of the experimental error. This is due to a tilt of the g_3 main peak axis, [8] i.e. to a tendency of the angles larger than the average to have bond lengths longer than the average. The smaller correlation value found for the a-Si:H case corresponds to a reduced extension of main peak along the θ axis and is a further confirmation of the structural ordering process.

REFERENCES

- 1] J. F. Grackzyk, Phys. stat. sol (a) **55**, 231 (1979); R. Bellissent, A. Chenevas-Paule, P. Chieux, A. Menelle, J. Non-Cryst. Solids **77&78**, 213 (1985).
- 2] W. Schülke, Phyl. Mag. B **43**, 451 (1981).
- 3] G. Etherington, A. C. Wright, J. T. Wenzel, J. C. Dore, H. J. Clarke, and R. N. Sinclair, J. Non-Cryst. Solids **48**, 265 (1982).
- 4] P. J. Durham, J. B. Pendry and C. H. Hodges, Sol. State Comm. **38**, 159 (1981); M. Benfatto, C. R. Natoli, A. Bianconi, J. Garcia, A. Marcelli, M. Fanfoni, and I. Davoli, Phys. Rev. B **34**, 5774 (1986); M. F. Ruiz-Lopez, M. Loos, J. Goulon, M. Benfatto, C. R. Natoli, Chem. Phys. **121**, 419 (1988).
- 5] A. Bianconi, A. Di Cicco, N.V. Pavel, M. Benfatto, A. Marcelli, C.R. Natoli, P. Pianetta, and J. Woicik, Phys. Rev. B **36**, 6426 (1987).
- 6] A. Filipponi, F. Evangelisti, M. Benfatto, S. Mobilio and C.R. Natoli, Phys. Rev. B **40** 9636 (1989).
- 7] M. Benfatto, C.R. Natoli, and A. Filipponi, Phys. Rev. B **40** 9626 (1989)..
- 8] A. Filipponi, A. Di Cicco, M. Benfatto and C.R. Natoli, proc. of the ICALS 13 (Asheville, U.S.A., 1989), to be published as a special issue of J. Non-Cryst. Solids.
- 9] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).
- 10] R. Biswas, G. S. Grest, and C. M. Soukoulis, Phys. Rev. B **36**, 7437 (1987). R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988).
- 11] A. Filipponi, E. Bernieri and S. Mobilio, Phys. Rev. B **38**, 3298 (1988).
- 12] A. Filipponi, Phys. Rev. B **37**, 7027 (1988).