Comment on "Boson peak in amorphous silicon: A numerical study"

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Based on molecular-dynamics simulations using the Stillinger-Weber interatomic potential, Finkemeier and von Niessen recently proposed that the presence of the Boson peak in *a*-Si can be attributed to coordination defects [F. Finkemeier and W. von Niessen, Phys. Rev. B **63**, 235204 (2001)] and claimed agreement with earlier simulation results for models of *a*-Si with voids [S. M. Nakhmanson and D. A. Drabold, Phys. Rev. B **61**, 5376 (2000)]. In this Comment, we clarify this issue and suggest that (i) the atomistic models of Finkemeier and von Niessen do not represent realistic amorphous silicon and (ii) the results for the models with voids *do not* support the hypothesis that coordination defects are the main cause of the appearance of the Boson peak in this material.

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In a recently published paper, Finkemeier and von Niessen[1] present a study of the low-frequency vibrational properties of model *a*-Si. Using simulation cells of up to 64 000 atoms, created with a method based on the bond-switching algorithm of Wooten, Winer, and Weaire[2] (WWW) and relaxed with the Stillinger-Weber (SW) potential,[3] they conclude that the emergence of a peak in the low-frequency region of the $g(\omega)/\omega^2$ curve, where ω is the phonon frequency and $g(\omega)$ is the vibrational density of states (VDOS), is due to the increasing concentration of coordination defects in their models. This conclusion is based on the deviation of the models's vibrational properties from Debye's theory, which Finkemeier and von Niessen (FvN) associate with the Boson peak found in covalent glasses. According to the authors, the hypothesis of a ''coordination defect'' origin of the Boson peak is supported by previous calculations of void-related vibrational properties of high-quality *a*-Si models performed by some of the authors of this paper.[4]

In this Comment, we show that (i) the models used by FvN are based on a misconception about the implementation of the WWW algorithm, are physically unrealistic, and show structural properties in qualitative disagreement with experiment and the current state-of-the-art models; and (ii) FvN have misinterpreted the results of Ref. 4, which actually disagree with their findings, thus undermining the connection between coordination defects and the Boson peak in *a*-Si. The main purpose of this Comment is therefore to underline the importance of using realistic structural models (as gauged by direct comparison to structural, electronic, and vibrational properties experimentally observed) in the study of controversial topics such as the Boson peak.

In the last few years, a number of developments have made it easier to generate high-quality models[5–8] of *a*-Si and many realistic models are now available. Regrettably, this progress has not been noted by all the practitioners in the field and models with unacceptable structural properties are still sometimes being used to study features of this material. The FvN models, for example, suffer from an incorrect implementation of the WWW bond-switching algorithm, which seriously impacts the quality of the resulting models. The original WWW papers (see Ref. 9, in particular) explicitly stress the need to anneal the structure through a series of Metropolis acception/rejection moves at finite temperature, which ensures low residual strain in a model. The models used by FvN, on the contrary, are generated at an effective infinite temperature and all moves are accepted until the structure looks ''disordered enough.'' The absence of finite-temperature annealing leads to two consequences:[10] (i) in order to keep the structure even remotely physical, the number of bond switches must be limited to 0.2–0.25 switches per atom leaving, unavoidingly, traces of crystallinity in a model—this compares to thousands of tentative and tens of accepted bond switches per atom used in Ref. 8; (ii) because the strain is not relaxed, the final structure shows wide bond angle and coordination distributions, a coordination number far away from the experimental value, and an electronically conducting model. For example, the experimental width of the bond-angle distribution, as measured by Laaziri *et al.*[11] is between 9.6° and 10.4° and that of the 4096-atom model of Djordjević, Thorpe, and Wooten (DTW), generated using the correct WWW algorithm, is 10.5°–11°. The disordered FvN models, by contrast, display a bond-angle distribution between 16° and 18°, which indicates a high degree of strain in the models.

The imperfect amorphization is also illustrated by the fact that the FvN models with 0.1–0.15 switches per atom still display clear traces of crystallinity. As the number of bond switches is increased, the deformations due to the strain hide the crystallinity of the networks but do not lead to an amorphous network as defined by the continuous-random-network

model. The number of coordination defects obtained after relaxation with the SW potential reaches 20–30 at %, an unphysical value: experimental electron-spin-resonance measurements find a density of defects between 0.1% and 1.0%,[12] while current continuous-random-networks models have between 0% and 2% coordination defects.

The use of the SW potential for relaxing a strained configuration is also questionable. This potential, which was first introduced in 1985, has been known to lead to amorphous structures that are strongly overcoordinated.[6,13] In recent years, new empirical potentials such as the environment-dependent interatomic potential (EDIP) (Ref. 7) and a ''modified'' version of the SW potential (mSW), explicitly fitted to the vibrational spectrum of amorphous silicon,[14] have been introduced that describe the amorphous phase in a much more satisfactory manner. Contrary to what happens with the original SW, structures prepared using the WWW algorithm and relaxed with EDIP or mSW remain essentially fourfold coordinated and have structural and vibrational properties ranging from good to excellent compared to experiment.

We now turn to the interpretation of the results of Ref. 4. In these calculations of vibrational and thermal properties of *a*-Si, we used the 4096-atom DTW model, which was relaxed with EDIP. The VDOS and the specific head $C(T)$ for the model were computed directly from the dynamical matrix, taking finite-size effects into account. These calculations were repeated for models with voids of different sizes, prepared by removal of a cluster of atoms from the network and subsequent relaxation, which lead to an atomic density of coordination defects ranging from 0.39% to 1.75%. A plot of $C(T)/T^3$ vs T for temperature range of 0–100 K shows a systematic bump at temperatures of 1–30 K, *independent* of the presence or absence of voids in our models (see Fig. 2 in Ref. 4).

The results obtained for these models provide, therefore, no evidence that coordination defects are the cause of the Boson peak in the vibrational spectrum of *a*-Si. The conclusions of FvN are most probably an artifact of the unphysically high defect concentrations in their models. This does not mean that calculations of FvN are wrong: obviously there exist many different mechanisms that could be responsible for an upward or downward shift of the vibrational states's frequencies in a model, thus creating deviations from $g(\omega)=\alpha\omega^2$ or $C(T)=\beta T^3$ law, and changing the average coordination may be one of such mechanisms. The problem, however, is that this particular mechanism is not an admissible solution for *a*-Si, as we showed previously, the small change in the density of coordination defects for realistic models of this material does not significantly change the non-Debye behavior of $C(T)$ at low temperatures.

To summarize, we demonstrated that the conclusions presented in a recent paper by Finkemeier and von Niessen are based on the use of models prepared with an improperly implemented version of the WWW bond-switching algorithm, which results in highly strained structures with likely traces of crystallinity. The further relaxation of the models with an empirical potential that is known to produce overcoordinated disordered networks leads to configurations exhibiting poor and unrealistic structural and vibrational properties as compared with experimental results for *a*-Si. The use of such models invalidates the conclusions of FvN regarding the origin of the Boson peak in this material. Our interpretation of FvN's results is supported by recent calculations made by some of us[8] on high-quality models of *a*-Si, relaxed with a realistic interatomic potential, and preserving the low strain and fourfold coordination of the models. Analyzing the trends in our models, as voids are introduced, we find no change in the low-temperature behavior of the vibrational spectrum as a function of coordination, contradicting directly to the conclusions of FvN.

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