Intense small wave-vector scattering from voids in amorphous silicon: A theoretical simulation

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Voids of various sizes have been introduced into amorphous-silicon models that were generated with molecular-dynamics simulations. The presence of the voids leads to a rapidly increasing structure factor for wave vectors below 1 Å^{-1} that is similar to the intense small-angle scattering observed in experiments. The voids cause only small changes in the vibrational densities of states. The presence of voids decreases the local strain in the *a*-Si networks, leading to a substantial reduction in the number of five-coordinated defect sites and a somewhat lower bond-angle strain from the *a*-Si model without voids. By comparing the properties of voids in crystalline and amorphous structures, we find the effect of decreasing the bond-angle disorder is to make the TO peak of the densities of states narrower and stronger, in agreement with Raman measurements.

I. INTRODUCTION

A universal feature of amorphous solids is the presence of voids or macroscopic inhomogeneities in the disordered structure. For amorphous semiconductors the characteristics of the voids are strongly dependent on the growth conditions. Structural inhomogeneities such as voids are commonly believed to result in the density of amorphous silicon or amorphous germanium being lower than their corresponding crystalline phases. The coarse microstructure and presence of voids in amorphous-silicon films can be imaged with electron microscopy. The characteristics of voids in pure and hydrogenated amorphous silicon have been inferred from intense small-angle scattering of neutrons,[1,2] electrons,[3] and x rays.[4,5] These experiments[1–5] measured a static structure factor $S(q)$ displaying a rapid increase for wave vector less than 1 Å^{-1}. This intense small-angle scattering was interpreted as due to a distribution of voids.

In many respects the small-angle scattering is the only quantitative probe of the microstructure of amorphous films, and is an extremely valuable tool in identifying the changes in the film microstructure after processing steps such as annealing or light illumination. In studies of the Staebler-Wronski[6] effect, for example, Chenevas-Paule *et al.*[2] have inferred from small-angle neutron scattering that illumination of *a*-Si:H with visible light leads to microstructural changes at a 100-Å scale that are reversible upon annealing.

The small-angle scattering is a measure of the long-wavelength density fluctuations in the amorphous material. If this scattering is assumed to be due to voids that can be represented by an average radius of gyration R_G, the $q \rightarrow 0$ scattering intensity is given by the Guinier relation,[7]

$$S(q)=S_0\exp(-q^2R_G^2/3) . \quad (1)$$

For small-angle-scattering data, Guinier plots of $\ln[S(q)]$ versus q^2 reveal approximate linear relationships over ranges of q, from which radii of gyration ranging from 270 to 5 Å have been estimated.[1–5] Although this intense small-angle scattering has been seen with a number of different probes, there has been little theoretical modeling of this scattering. In fact, it is not known if theoretical structural models can support the presence of voids and can account for this small-angle scattering in *a*-Si.

Recently a number of *a*-Si structural models have been computer generated with Monte Carlo[8,9] or molecular-dynamics simulations.[10–15] These *a*-Si models have radial distribution functions, bond-angle distributions, phonon densities of states, and the infrared and Raman-scattering cross sections that compare well with experiment. However, the static structure factor for these models approaches zero continuously as $q \rightarrow 0$. In this paper we investigate whether theoretical *a*-Si models can describe the intense small-angle scattering found experimentally.

II. RESULTS FOR *a*-Si

The investigations in this paper are based on the class of *a*-Si models generated by Biswas, Grest, and Soukoulis[10] (BGS) from molecular-dynamics simulations of quenching a melt, resulting in N-atom models ($N=512$ and 2000) with periodic boundary conditions. The molecular-dynamics simulations were performed with separable two- and three-body Si interatomic potentials developed by Biswas and Hamann,[16] and resulted in *a*-Si structures. This Si interatomic potential[16] is more complicated than is necessary for calculating vibrational properties, and its parameters were not optimized to fit vibrational data. For determining phonon densities of states, we adopted the Keating model with bond-stretching and bond-bending force constants (α and β). Monte Carlo calculations at zero temperature were used to relax the BGS networks with the Keating potential[17] and Keating parameters of $\alpha=42.1$ N/m and $\beta/\alpha=0.16$. The change in the atomic positions was minimal as a result of this additional relaxation step, which led to a local minimum with the Keating potential energy.

The Keating-model calculations of the vibrational densities of states of the *a*-Si models[18,19] compares well with experiment[20] (Fig. 1), describing the TA and TO peaks well. The coordination defects in these models have led to predictions[18] for localized vibrational modes at both high and low frequencies. The calculated structure factor $S(q)$ (Fig. 2) smoothly approaches zero as $q\rightarrow 0$, illustrating the homogeneity of the amorphous network.

The columnar growth of *a*-Si films[21–25] often leads to void structures that are somewhat ellipsoidal in nature. Due to the finite size of our models, columnar voids are difficult to model. As a first step to understanding the properties of voids in *a*-Si, we have chosen to study the properties of simple spherical void structures, which can be easily generated. As the results of this paper indicate, many experimental features of the scattering can be understood from the simple spherical multivoid structures. We have also performed calculations for simple ellipsoidal void shapes and found the vibrational and scattering properties to be qualitatively similar to that for spherical voids.

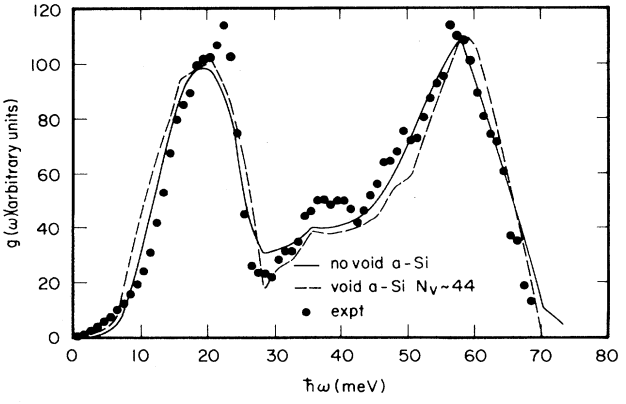

FIG. 1. Vibrational densities of states for *a*-Si models—without voids ($N=512$ atoms, solid line), with voids of average size 44 atoms, and with $N=380$ atoms. Experimental points are from Kamitakahara *et al.* (Ref. 18).

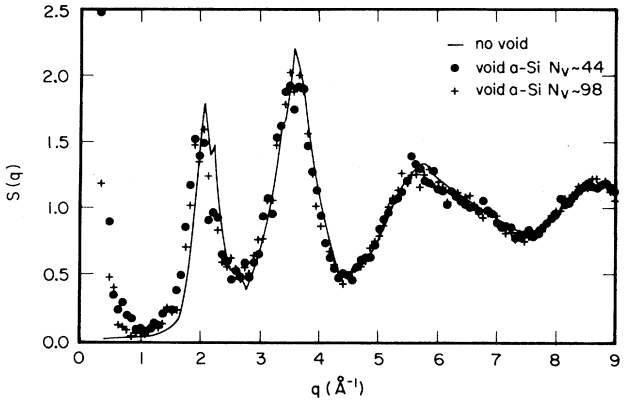

FIG. 2. Static structure factor $S(q)$ for *a*-Si models without voids (solid line) compared with *a*-Si models with void sizes of N_v atoms (points).

We found that a simple way to generate approximately symmetrical voids in the amorphous network was to remove a cluster starting with an atom selected at random and its shell of first neighbors. The neighbors of this first shell were removed and the process extended up to m shells around the central site. With this simple procedure much fewer bonds are broken than by removing atoms within some prescribed volume. By choosing the centers of the voids to be sufficiently far apart a number of nonoverlapping voids were then constructed.

The void structures were relaxed by a steepest-descent relaxation with the two- and three-body Si interatomic potential,[16] which led to a rebonding of atoms at the void surfaces. The Keating potential was not used in this step since it preserves the local coordination of the atoms. Relaxation of the *a*-Si networks with the Si interatomic potential was a much more efficient way to achieve rebonding at the void surfaces. After the steepest-descent relaxation we equilibrated the *a*-Si models with the Keating potential with Monte Carlo calculations at zero temperature, which resulted in a minimal change in atomic positions. The Keating equilibration calculation was performed at different densities, and we found that somewhat lower atomic volumes were energetically favored for the networks with voids. The equilibration with the Keating model was necessary to consistently compare vibrational densities of states calculations with the previous results for *a*-Si models without voids. We stress that the models with voids are not hypothetical high-energy configurations, but are energetically competitive with the starting amorphous network. The *a*-Si model 6 (without voids) had an energy of -3.377 eV/atom compared to -3.398 and -3.388 eV/atom for models 7 and 8, which had voids. These energies were computed after the steepest-descent relaxation step with the two- and three-body interatomic potential.

The resulting *a*-Si models showed a substantial increase of dangling bonds and a decrease of five-bonded sites

TABLE I. The structural characteristics and local disorder of the Si models with voids.

a-Si model	No. of atoms, N	Average void size $\langle N_v \rangle$	No. of voids	No. of shells, m	$(\Delta\theta)_{rms}$ (deg)	$(\Delta r)_{rms}$ (Å)
1	512	0	0		11.6	0.044
2	414	98	1	4	10.96	0.043
3	380	44	3	3	10.53	0.040
4	429	17	5	2	10.94	0.044
5	463	5	10	1	11.19	0.046
6	2000	0	0		10.92	0.054
7	1696	43	7	3	10.56	0.052
8	1565	87	5	4	10.83	0.059
c-Si model						
1	407	35	3	3	6.78	0.032
2	429	87	1	4	4.75	0.034

from the original network that had no voids. Average void sizes (N_v) of 17, 44, and 98 atoms were constructed with values of m of 2, 3, and 5, respectively (Table I). The vibrational densities of states (Fig. 1) displayed only small changes with the introduction of the voids. A noticeable feature is the loss of modes between 28 and 32 meV for the networks with voids, so that the density of states (DOS) has a much deeper minimum after the TA peak (Fig. 1). Consequently a more well-defined peak at 35 meV appears, which is the analog of the crystalline LA peak. We interpret the excitations between 28 and 32 meV to be analogous to the longitudinal-acoustic phonons of the crystal with wavelengths in the range (2–4)a, where a is the crystalline lattice constant (5.431 Å). These modes are unable to propagate through the network when the spacing between the voids is of the order of the wavelength of these modes, leading to a decrease of such modes for the networks with voids. In fact, the introduction of voids leads to calculated DOS's that are in qualitatively better agreement with the experimental data[20] than that of the original network.[18,19] The density of the a-Si network with the voids is somewhat less than that of c-Si, in agreement with experimental measurements of the density of a-Si. In contrast, the original a-Si model had a higher density than c-Si.

The strain in the amorphous network is somewhat relieved by the presence of voids, as illustrated by the somewhat lower bond-angle deviations for the networks with voids (Table I). It is plausible that the very similar bond-angle and bond-length disorder leads to little overall change in the TA or TO vibrational DOS peaks due to voids.

The relief of the local strain by the voids is also illustrated by the substantial decrease in the number of five-coordinated atoms for the networks with voids (Table II). The decrease in five-coordinated sites to a density below 1% (from an initial density of 10%) is most evident in models with large numbers of voids (models 2 and 3, Table II). As is evident from Table II, there is a large increase in the number of dangling bonds, primarily at the void surfaces, in the networks with voids. Pantelides has proposed[26] that the motion of five-coordinated defect sites is an important pathway for atomic diffusion in a-Si. The substantially reduced density of five-coordinated sites eliminates this diffusion path in the networks with voids. This feature is qualitatively in agreement with the absence of H diffusion in rf-sputtered a-Si:H films that have voids and a high density of dihydride and trihydride species.[27]

The most significant effect of the voids is to cause a rapid increase in the static structure factor $S(q)$, for wave vectors less than 1 $Å^{-1}$ (Fig. 2), with negligible changes for larger q. The rapidly increasing structure factor below 1 $Å^{-1}$ is seen for average void sizes of 98 and 44

TABLE II. The number of atoms N_i with coordination i in the a-Si models with voids, compared with the a-Si model without voids.

a-Si model	No. of atoms	Void size $\langle N_v \rangle$	No. of voids	N_2	N_3	N_4	N_5
1	512	0	0	1	34	425	52
2	414	98	1	2	69	338	5
3	380	44	3	2	101	276	1
4	429	17	5	1	77	348	3
5	463	5	10	1	50	386	26

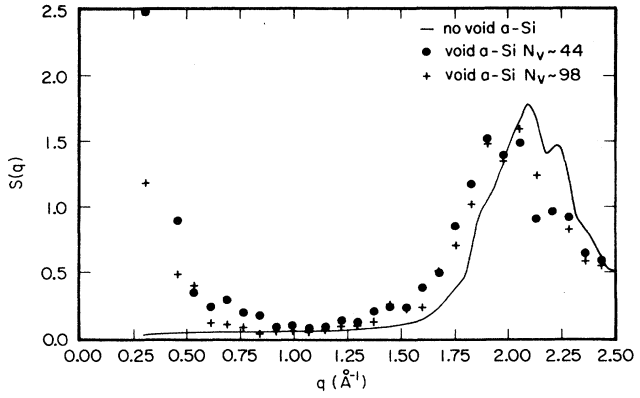

FIG. 3. Small wave-vector region showing the rapidly increasing structure factor for a-Si models with average void sizes of N_v atoms (points), compared to the a-Si model without voids.

atoms (Fig. 3). The increase in $S(q)$ is barely perceptible for the 17-atom voids and not shown separately in Fig. 3. The finite size of the periodic unit cell leads to a cutoff for the smallest wave vector in the calculation, which is 0.28–0.30 Å^{-1}, for the networks in Fig. 3.

In Fig. 4 we plot our results for $S(q)$ with an average void size N_v of 44 atoms, together with the experimental results of Postol *et al.*[1] The agreement is impressive in the entire q region. For very low q our calculated $S(q)$ is larger than experiment. It is worth noting that the second peak of $S(q)$ is higher than the first peak, similar to experiment. Amorphous silicon models from Monte Carlo simulations[8,9] had the first peak of $S(q)$ much higher than the second peak,[10] indicating excessive long-range order in the Monte Carlo models. Calculated $S(q)$ for a-Si models compare well with experiment in the large-q region ($q>1.5$ Å), as discussed by other authors.[12,28]

A Guinier plot of $\ln[S(q)]$ as a function of q^2 (Fig. 5) for the void structures constructed from the $N=512$ model reveals approximate linear relationships for $q<0.8$ Å^{-1}, although there is a considerable scatter. The scatter

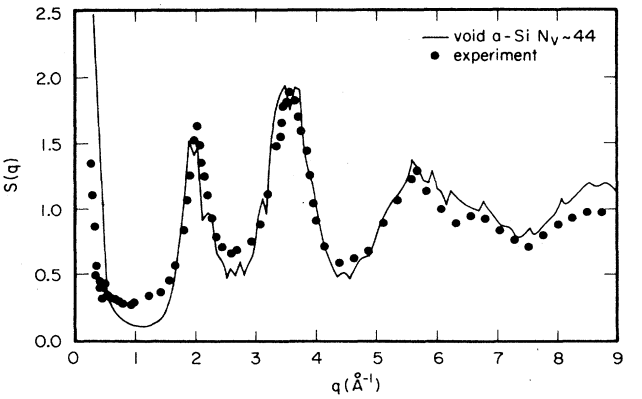

FIG. 4. Structure factor $S(q)$ for a-Si model with voids compared to experimental data from Postol (Ref. 1). The results for $S(q)$ for $N_v=98$ were very similar and not shown separately.

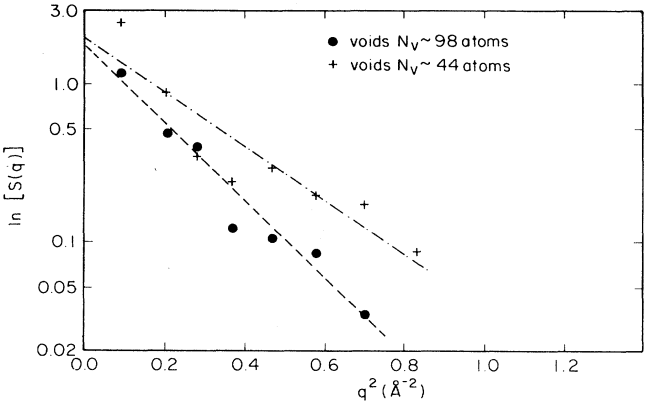

FIG. 5. Guinier plot of the logarithm of the structure factor as a function of q^2. Only the rapidly increasing $S(q)$ due to scattering from voids for $q<0.9$ Å is shown. Approximate straight-line fits to the calculations are shown.

in Fig. 5 may be a result of the nonspherical nature of the voids since the removed atoms are not distributed symmetrically around the central site. We expect that the scatter would be less significant for larger void sizes where the variations at the boundary have less effect on the void size. From the slopes in Fig. 5, and assuming Eq. (1) holds, we extract void radii (R_G) of 4.53 Å ($N_v=98$) and 3.94 Å ($N_v=44$), which are somewhat smaller than the void radii of 5.26 and 4.16 Å expected for crystalline Si (i.e., the fourth- and third-neighbor distances) at the same density as our a-Si model. The relaxation of the structure may be lead to a compression in the volume of the individual voids.

We confirmed that the large scattering was independent of the amorphous network used by calculations for the larger 2000-atom network, where a larger number of voids (of 43- and 87-atom size) was possible (Table I). Owing to the large size of the dynamical matrix, the phonon DOS could not be explicitly calculated for this network. The calculated $S(q)$ (Fig. 6) shows very similar

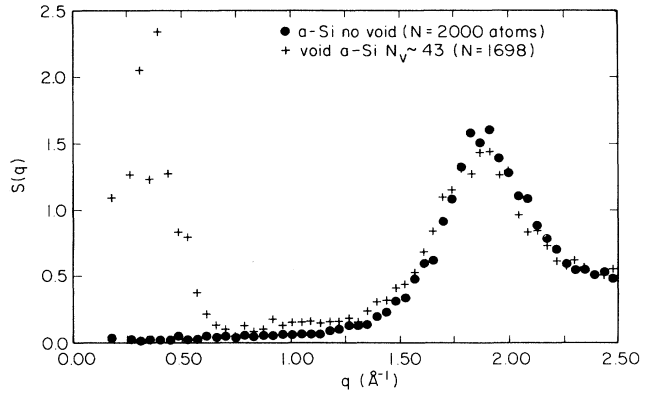

FIG. 6. Small wave-vector region showing the rapidly increasing structure factor for a-Si models with average void size N_v, compared to the a-Si model without voids (with $N=2000$ atoms). The void structure were derived from the $N=2000$ atom a-Si model.

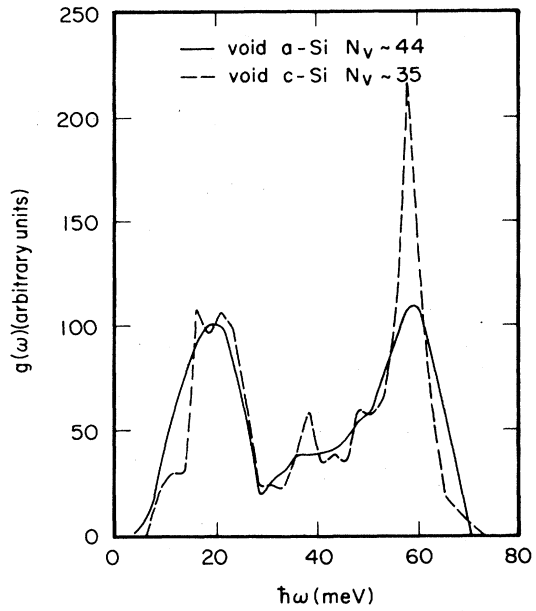

FIG. 7. Vibrational densities of states for *a*-Si models with voids (rms bond-angle distribution 10.5°), compared to the model derived from voids in a *c*-Si structure (rms bond-angle distribution 6.8°).

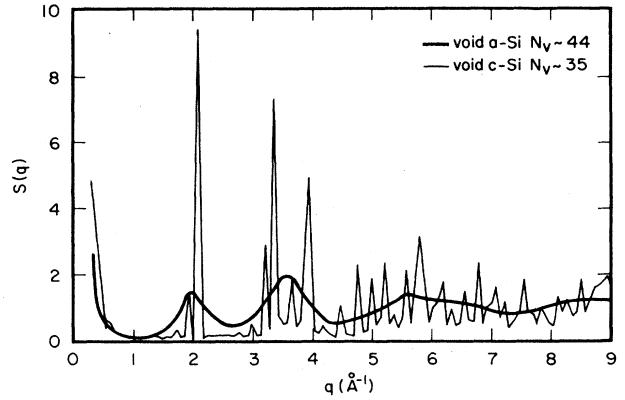

FIG. 8. Static structure factor of *a*-Si model with voids compared to the model derived from voids in a *c*-Si structure.

trends as the smaller networks, including an abrupt increase for $q < 0.75$ Å^{-1}. The larger scatter of the $S(q)$ in the small-q region may be a result of substantial variations in the void size.

The large scattering at small wave vectors can also be seen in the dynamic structure factors of modes below ~10 meV. The low-frequency localization[18] seen in the *a*-Si models is still present but somewhat inhibited in the models with voids. In a number of the void models we found that the single atoms that participated in the low-frequency resonant modes have been removed during the construction of the voids. Also, the generation of the voids has reduced the local strain that led to the strong low-frequency localization.

III. COMPARISON OF VOIDS IN *c*-Si AND *a*-Si

Recent Raman measurements by Lannin[28] on amorphous Ge films deposited by sputtering at different temperatures showed that the higher-temperature films that had greater local order had a narrower and stronger TO band. It was proposed that the width of the TO vibrational band[28,29] or the ratio of the TO and TA peak heights[28] could serve as a measure of the local order of the amorphous material, and thus provide a convenient characterization tool of the film microstructure. In the limit of crystalline silicon, the TO band is very sharp with a TO to TA peak ratio of ~2.

We attempted to test the sensitivity of the vibrational spectra to the degree of disorder in *a*-Si. We found that a convenient way to decrease the disorder from that of our *a*-Si models was to make models of voids in *c*-Si structures. We generated voids in a crystalline diamond Si structure (with a 512-atom supercell), and relaxed the resulting void structures with steepest-descent calculations followed by Monte Carlo relaxation, as in the amorphous case. This resulted in two void structures with different void sizes (Table I). The bond-angle distributions in these structures ranged between 5° and 7° (Table I), due to the atoms at the surface of the void having an approximately amorphous environment, while atoms in the bulk region had distorted tetrahedral coordination.

The vibrational densities of states for the void model derived from *c*-Si are compared with that of an *a*-Si void model (Fig. 7). We confirm the Raman findings that the TO peak is the most sensitive probe of the local disorder and shows a pronounced narrowing to ~5.5 meV in our model that has a rms bond-angle distribution of 6.8°, from its original value of ~15.4 meV. The ratio of the TO to TA peak heights can serve as an index of the crystallinity of the material. As expected, the LA- and LO-derived features are considerably sharper in the *c*-Si model with voids which may have many features similar to that of microcrystalline silicon. The TA band is least sensitive to the variation of the local disorder. The static structure factor $S(q)$ (Fig. 8) also shows a rapid rise for wave vectors below 1 Å^{-1}, but has sharp features at larger q.

In conclusion, we have generated models of amorphous silicon that contain voids of various sizes. These *a*-Si models give rise to intense small wave-vector scattering similar to the experimental data. We confirm that the Guinier scattering form is approximately valid. We expect the theoretical calculations to be smoother for calculations with larger voids. In future work we plan to study the vibrational properties and structure factors from hydrogen on the void surfaces.

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[1]T. A. Postol, C. M. Falco, R. T. Kampwirth, I. K. Schuller, and W. B. Yellon, Phys. Rev. Lett. **45**, 648 (1980).
[2]A. Chenevas-Paule, R. Bellissent, M. Roth, and J. I. Pankove, J. Non. Cryst. Solids **77-78**, 373 (1986).
[3]A. J. Craven, A. J. Patterson, A. R. Long, and J. I. B. Wilson, J. Non. Cryst. Solids **77-78**, 217 (1986).
[4]P. D'Antonio and J. H. Konnert, Phys. Rev. Lett. **43**, 1161 (1979).
[5]N. J. Shevchik and W. Paul, J. Non. Cryst. Solids **16**, 55 (1974).
[6]D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[7]A. Guinier, G. Fournet, C. B. Walker, and K. L. Yudowitch, *Small Angle Scattering of X-rays* (Wiley, New York, 1955).
[8]F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).
[9]K. Winer, Phys. Rev. B **35**, 2366 (1987).
[10]R. Biswas, G. S. Grest, and C. M. Soukoulis, Phys. Rev. B **36**, 7437 (1987).
[11]K. Ding and H. C. Andersen, Phys. Rev. B **34**, 6987 (1986).
[12]M. D. Kluge, J. Ray, and A. Rahman, Phys. Rev. B **36**, 4234 (1987).
[13]W. D. Luedtke and U. Landman, Phys. Rev. B **37**, 4656 (1988).
[14]R. Car and M. Parinello, Phys. Rev. Lett. **60**, 204 (1988).
[15]P. Kelieres and J. Tersoff, Phys. Rev. Lett. **61**, 562 (1988).
[16]R. Biswas and D. R. Hamann, Phys. Rev. B **36**, 6434 (1987); Phys. Rev. Lett. **55**, 2001 (1985).
[17]P. N. Keating, Phys. Rev. **145**, 637 (1966).
[18]R. Biswas, A. M. Bouchard, W. A. Kamitakahara, C. M. Soukoulis, and G. S. Grest, Phys. Rev. Lett. **60**, 2280 (1988).
[19]A. M. Bouchard, R. Biswas, W. A. Kamitakahara, C. M. Soukoulis, and G. S. Grest, Phys. Rev. B **38**, 10499 (1988).
[20]W. A. Kamitakahara, C. M. Soukoulis, H. R. Shanks, U. Buchenau, and G. S. Grest, Phys. Rev. B **36**, 6539 (1987).
[21]J. E. Yehoda, B. Yang, K. Vedam, and R. Messier, J. Vac. Sci. Technol. A **6**, 1631 (1988), and references therein.
[22]*The Physics of Hydrogenated Amorphous Silicon,* edited by D. Joannopoulos and G. Lucovsky (Springer-Verlag, New York, 1984).
[23]J. Shinar, R. Shinar, S. Mitra, M. L. Albers, H. R. Shanks, and T. D. Moustakas, in *Amorphous Silicon Semiconductors—Pure and Hydrogenated,* Mater. Res. Soc. Symp. Proc. No. 95, edited by A. Madan, M. Thompson, D. Adler, and Y. Hamakawa (MRS, Pittsburgh, 1987), p. 183.
[24]R. Messier and R. C. Ross, J. Appl. Phys. **53**, 6220 (1982).
[25]J. S. Lannin, in *Disordered Semiconductors,* edited by M. Kastner and G. A. Thomas (Plenum, New York, 1987), p. 283.
[26]S. Pantelides, Phys. Rev. Lett. **57**, 2979 (1986); **58**, 1344 (1987).
[27]J. Shinar, R. Shinar, S. Mitra, and J. Y. Kim (unpublished).
[28]J. S. Lannin, J. Non-Cryst. Solids **97-98**, 39 (1987).
[29]L. Guttman, Phys. Rev. B **23**, 1866 (1981).
[30]D. Beeman, R. Tsu, and M. F. Thorpe, Phys. Rev. B **32**, 875 (1985).