Elastic properties of amorphous Si and derived Debye temperatures and Grüneisen parameters: Model calculation

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Calculations, based on the Stillinger-Weber (SW) interatomic-potential model and the method of long waves, are presented for the elastic properties of amorphous Si (a-Si) and for pressure derivatives of the elastic constants of crystalline Si. Several models of a-Si, relaxed on the basis of the SW potential, are considered, and the external stresses that are associated with these models are evaluated using the Born-Huang relations. The elastic constants appear to obey the isotropy conditions to within a reasonable accuracy and are also consistent with other predictions based on the SW potential at finite temperature obtained by Kluge and Ray. Estimates of the pressure dependence of the elastic constants, Debye temperature, and Grüeisen parameter for a-Si are also provided on the basis of these calculations.

I. INTRODUCTION

It is useful to examine the microscopic basis of the elastic constants in amorphous Si (a-Si) since it is difficult to obtain them experimentally because samples are in the form of thin films. Single experimental values of the Young's modulus[1] and of the Rayleigh-wave velocity[2] have been provided for separate (amorphized) samples, both stated to have a density 0.95 times the crystalline density. In addition, Rayleigh-wave velocities in an amorphized sample were measured as a function of temperature.[3] Since there could be important sample-dependent effects, a combined experimental and theoretical study of elastic constants could also help characterize structures. Indeed, it is found that quite different results are obtained for (low-density) sputtered and amorphized materials.[3]

Elastic properties of a-Si can be estimated through the use of structural and interatomic potential models. One of the first attempts at such an estimate was that of Guttman,[4] who made use of the Keating potential,[5] which is known to give accurate *crystalline* elastic constants. This estimate was based on models with periodic boundary conditions and with relatively few independent atomic positions in comparison to recent models. Guttman used the method of homogeneous deformation (MHD), whereby he imposed various elastic strains and computed their effect in the potential energy. Earlier, Steinhardt *et al.*[6] presented a MHD elastic constant study for 519- and 210-atom continuous-random-network (CRN) models having surface atoms (of less than full coordination). They applied their study to a-Ge, but their results are easily transferable to a-Si. More recently, Kluge and Ray[7] (KR) have made use of molecular-dynamics (MD) techniques and the fact that the elastic constants are linear-response functions. (A generalization of the theory

to the case of initial stresses has also been given.)[8] Kluge and Ray obtained elastic constants of 216-atom models, also with periodic boundary conditions, of a-Si at $T=294$ and 478 K. Their method does not take into account quantum effects, but it does take into account anharmonicity to all orders. Guttman's results yield static-lattice elastic constants, i.e., $T=0$ K results in the absence of zero-point-energy effects. Both methods properly include internal-displacement contributions to the elastic constants. The estimate of KR is also consistently based on the Stillinger-Weber[9] (SW) potential, since the structure as well as the (MD) computed elastic constants are determined on the basis of that potential.

It should also be noted that the SW potential does not represent the crystalline elastic constants as precisely[10,11] as the Keating potential does (which presumably can be explained in terms of the difference in values of the ratio of the bond-angle to bond-length force constants between the two potentials).[12] Nevertheless, KR (Ref. 7) pointed out that although the experimental amorphous-state elastic constants also do not appear to be accurately given by the SW potential, the SW potential correctly predicts differences between (averaged) crystalline and amorphous elastic constants. We also mention that Cowley[10] has compared values of selected elastic and vibrational properties of crystalline Si as calculated with a few recently proposed interatomic potentials and concluded that the SW potential gave best overall results.

In this paper we consider static-lattice elastic constants of a-Si on the basis of the SW potential and we consider several structural models consisting of 216 atoms as well as one of 1000 atoms. Our method of evaluation is the method of long waves,[13] which is applicable to crystals since it is based on a perturbation theory, in the wave vector, of the secular equations of lattice dynamics. However, models of a-Si can be regarded as crystal lat-

tices with large unit cells consisting of many basis atoms that are presumed to correspond to the amorphous material. (Of course, the "lattice" merely serves to implement periodic boundary conditions as the range of the interatomic forces is considered to be negligible in comparison with the "lattice" parameter.) Thus the method of long waves is directly applicable to these models, although the method will involve taking the inverse of a large real symmetric matrix, of order $3N-3$, composed of generalized force constants. The method of long waves and the other methods discussed above are fundamentally equivalent in the $T=0$ K limit. Finally, a recent[14] treatment of the method of homogeneous deformation that is more general than that given in Ref. 13 can be seen to be equivalent to the method of long waves in the $T=0$ K limit.

The Born-Huang relations,[13] which relate external stresses to elastic coefficients, $S_{ij,kl}$, are also examined in this paper. The models under consideration have been relaxed, using MD, with either the virial pressure being monitored,[15] which restricts the external stresses to $p=-\sum_{i=1}^{3}T_{ii}/3$, or the volume kept fixed. (Relaxation is accomplished by setting the total kinetic energy to zero every few hundred time steps.) Neither of these approaches ensures that the individual components, T_{ij}, of the stress tensor correspond to hydrostatic pressure conditions. Once the external stresses are known through use of the Born-Huang relations, the corresponding strains and strain energy can also be computed through a knowledge of the elastic constants. It is worthwhile to point out the existence of external stresses in the models which Guttman used. Guttman noted that the energy was not a relative minimum at the cubic-cell configuration, but instead at a finite value of strain for each strain component that was varied; reference states for the elastic constants were chosen to correspond to these relative minima, and hence different elastic constants correspond to different reference states in the work of Ref. 4.

We shall also obtain estimates of the pressure dependence of elastic constants of a-Si and crystalline Si on the basis of the SW potential. The latter is included for comparison because we are unaware of the availability of such calculations for the SW potential. Applications of our results to the low-temperature limits of the specific-heat Debye temperature and thermodynamic Grüneisen parameter are also made.

II. MODELS

We consider, primarily, three different 216-atom models of a-Si: (a) the model of Broughton and Li[16] (denoted model I in our calculations), which is the Wooten-Winer-Weaire (WWW) model[17] relaxed via the SW potential to a structure of zero virial pressure and static equilibrium; (b) a Kluge-Ray-Rahman (KRR) model[18] derived on the basis of the SW potential through a MD quench of the liquid state—the particular model transmitted to us corresponds to $T=471$ K; and (c) a model of Wooten[19] derived by the same procedure as was the WWW model, but with fourfold rings allowed. The

KRR model was relaxed at fixed volume in order to provide a structure (model II) in which the atoms are in static equilibrium. We performed two different relaxations on the basis of the Wooten model—one (model III) keeping the volume fixed at the crystalline value, i.e., the volume used by Wooten, and one (model IV) in which the (virial) pressure was also minimized, thereby allowing the cell volume (as well as the internal coordinates) to "relax." Models I and IV have number densities in SW units $(1/\sigma^3=[1/(2.091$ Å$)]^3)$ of 0.4545 and 0.4404, respectively. The density of model I is noted to be quite close to the crystalline density of 0.460 as well as to the density, 0.4527, of model II. We find that model III corresponds to a virial pressure of $p=4.078$ GPa. We also mention that models I and II are energetically lower than model IV by 0.02 in SW units/atom (1 SW unit$=3.4723\times10^{-12}$ erg), where, for the SW potential, the cohesive energy for crystalline Si is 2 SW units/atom.

In addition, we study a 1000-atom model (model V) recently introduced[20] in a calculation of thermal conductivity of a-Si. This model is quite closely related to model IV since they are both obtained by the same algorithm. Its density is 0.4396. Its potential energy is lower than that of model IV by 3×10^{-3} SW units/atom. Finally, it is remarked that the secular equations of lattice dynamics have been solved for all of the models considered here and it was found that models II (Ref. 21) and V (Ref. 20) have one small imaginary frequency each, and associated eigenvectors corresponding to fairly localized modes. These instabilities can be expected to have a negligible influence on the elastic properties of the models, at least within the framework of the calculations to follow.

We wish to point out that the models studied in this paper are substantially different from those recently introduced by Kwon et al.[22] The latter are appropriate to sputtered samples. They have low densities due to the presence of voids and are also characterized by low coordinations (3.5–3.7) in comparison to our models. In particular, the average coordinations are 4.037, 4.009, 4.009, 4.000, and 4.000 for models I–V, respectively. Here we have assumed a cutoff of 1.28σ as a criterion for coordination. This cutoff occurs in the tails of the first peaks of the radial distribution functions for all of our models, where the maxima of these peaks occur at interatomic distances within 2% of one another; the cutoff used by Kwon et al. was similarly chosen. It should also be pointed out that models IV and V are not perfectly fourfold coordinated as a few threefold and fivefold coordinations exist in these models.

III. EXTERNAL STRESSES

The Born-Huang expressions for external stresses are

$$S_{ii}-S_{jj}=[jj,ii]-[ii,jj], \quad i,j=1,3 \tag{1}$$

and

$$S_{ij}=[jj,ji]-[ij,jj], \quad i,j=1,3 , \tag{2}$$

where

$$[ij,kl]=-\frac{1}{2V}\sum_{\kappa,\kappa'}\sum_{m}\Phi_{ij}\begin{bmatrix}m\\\kappa\kappa'\end{bmatrix}x_k\begin{bmatrix}m\\\kappa\kappa'\end{bmatrix}x_1\begin{bmatrix}m\\\kappa\kappa'\end{bmatrix} . \tag{3}$$

TABLE I. Stresses (in units of GPa).

Component	Model				
	I	II	III	IV	V
$S_{11}+p$	−0.26	0.37	−0.60	−0.26	0.16
$S_{22}+p$	0.02	0.09	0.91	0.68	0.09
$S_{33}+p$	0.24	−0.46	−0.32	−0.42	−0.25
S_{23}	0.01	−0.64	0.42	0.43	−0.22
S_{13}	−0.68	0.08	−0.48	−0.41	0.07
S_{12}	−0.34	−0.05	−0.49	−0.48	−0.07

Here, m is a unit-cell index, κ is a basis-atom index, the Φ_{ij}'s are the second-order coupling constants, and $x(^{m}_{\kappa\kappa'})$ refers to equilibrium position vectors.[13] Results are given in Table I for the various models considered here. It is evident that these models, which are based on cubic periodic boundary conditions and which have been relaxed to temperatures less than ~ 3 K, are under stresses ranging up to 0.2–0.9 GPa (1 GPa = 10 kbar), aside from the substitutional virial pressure of model III. The presence of these stresses is due to the cubic periodic boundary conditions that are imposed. Because internal stresses can be more easily "relieved" for a large model than for a small one, these external stresses were expected to depend on the size of the model, as was indeed found (compare the first four columns of the values in Table I with the fifth). Owing to the presence of these stresses, the elastic coefficients that enter into the elastic-wave equations (i.e., the $S_{ij,kl}$'s in the notation of Ref. 13) will not have the usual symmetry properties. It is most convenient in that case to quote elastic constants based on Lagrangian strain parameters, which enter into the quadratic and higher-order terms in the strain energy formally the same as do the ordinary infinitesimal strains in the cases of either zero stress or hydrostatic pressure.[23]

IV. ELASTIC CONSTANTS AND STRAIN ENERGIES

In Table II we give selected Lagrangian elastic constants, C_{ij}, for the models considered. (In our notation,

"C" denotes elastic constants based on Lagrangian strains and "c" those based on infinitesimal strains.) These elastic constants correspond to a single reference system with external stresses, S_{ij}, present. It is of interest to see how well these elastic constants obey the isotropy relation $C_{44}=(C_{11}-C_{12})/2$. The values of Table II show deviations from the less restrictive cubic, as well as isotropic, symmetry in various elastic-constant comparisons. Most likely, these deviations can be attributed to both the finite size of the models and the cubic periodic boundary conditions. As we have noted, those effects also lead to the isotropic-symmetry-breaking stresses of Table I. In fact, we have tried to explain the deviations from elastic isotropy, in the case of the 216-atom models, solely in terms of the above stresses using two of the three independent third-order elastic constants of an elastic continuum that enter into these considerations as adjustable parameters, but we could not obtain satisfactory results. Therefore we conclude that the deviations of our results from the isotropy relations is not primarily caused by the external stresses present, but, instead, by the finite nature of the models. Certainly the isotropy relations are seen to be better obeyed for model V than for the 216-atom models, as expected. Further, similar deviations from elastic isotropy, to results for models I–IV, for a 216-atom model were obtained in Ref. 7, despite the fact that the latter calculations correspond to a reference system for which the external stresses are zero.[24]

The calculations of Kluge and Ray yielded

TABLE II. Lagrangian elastic constants C_{ij} (in units of 10^{11} dyn/cm^2).

Selected components[a]	Model				
	I	II	III	IV	V
11	14.30	13.22	14.99	11.94	13.24
22	13.92	14.65	15.16	13.11	12.83
33	14.48	15.20	16.09	13.07	12.78
12	8.05	7.85	8.23	6.69	7.05
13	8.01	7.79	8.23	5.95	6.90
23	8.36	8.01	8.61	6.88	7.00
44	3.66	3.21	3.49	3.01	3.10
55	3.34	3.87	3.75	3.21	2.94
66	3.45	3.37	3.32	2.54	3.00
14	0.09	−0.08	0.32	0.56	−0.03
25	−0.06	0.27	−0.09	−0.28	0.17
45	−0.08	0.09	0.01	0.03	0.12
44−(11−12)/2	0.54	0.03	0.11	0.39	0.01

[a]The additional nine independent elastic constants that are not given here are similar in magnitude to the last four rows of values.

TABLE III. Isotropic parameters and strain energy per atom, e, of models. Isotropic parameters and strain energy (strain energies are based on strains resulting from stresses, $S_{ij} + p\delta_{ij}$, given in Table I) of models (values in parentheses represent maximum deviations from average values).

| | Model | | | | |
	I	II	III	IV	V
λ (10^{11} dyn/cm^2)	8.14(0.2)	7.88(0.2)	8.76(0.3)	6.51(0.6)	6.98(0.08)
μ (10^{11} dyn/cm^2)	3.26(0.5)	3.36(0.7)	3.12(0.4)	3.01(0.5)	3.00(0.1)
$10^{-4}e$ (SW units/atom)[a]	5.0	3.4	3.3	5.6	0.493
Debye temperature Θ_0 (K)	463	470	445	447	446

[a] 1 SW unit $= 3.4723 \times 10^{-12}$ erg.

$c_{12} = 8.3 \times 10^{11}$ dyn/cm^2 at both $T = 294$ and 478 K. They also yielded $c_{44} = 3.3$ and 2.7×10^{11} dyn/cm^2 at $T = 294$ and 478 K, respectively, and $c_{11} - 2c_{44} = 8.6$ and 8.0×10^{11} dyn/cm^2 at $T = 294$ and 478 K, respectively.[7] These results compare well with our values. As indicated above, the volume of model II corresponds to the $T = 471$ K volume. Ignoring the small volume difference between $T = 471$ and 478 K, the difference in elastic-constant values between model II and these $T = 478$ K values ought to reflect the combined effect of explicit temperature-dependent terms and of differences in resulting atomic coordinates when the potential energy is minimized and when the free energy is minimized. However, the observed differences in values are small and could be attributed[24] merely to the above-mentioned difference in reference states—our reference state corresponds to a cubic unit cell, whereas that of Ref. 7 does not.

It is well known that to first order in anharmonic effects the elastic constants are linear in T at high T and the linear extrapolation to $T = 0$ K yields the static-lattice elastic constants. The extrapolation to $T = 0$ K of KR's results yields $c_{12} = 8.3 \times 10^{11}$ dyn/cm^2 and $c_{44} = 4.2 \times 10^{11}$ dyn/cm^2. These values should be equivalent to those of model II plus a small volumetric correction, as model II corresponds to a small virial pressure (~ -0.3 GPa). Based on our estimate of pressure dependencies given in a following section, the correction to λ, i.e., c_{12}, is $\sim +0.15 \times 10^{11}$ dyn/cm^2 and that to μ, i.e., c_{44}, is negligible. Model II results and the above extrapolated values are then seen to compare favorably for c_{12}, but not for c_{44}, as the extrapolated value of c_{44} is somewhat too large. The latter difference, however, is well within estimated combined uncertainties of the calculations. Larger models will clearly be required to study this relationship in greater detail.

Next, we make use of the above values of elastic constants to estimate the strain energies associated with the external stresses that we have computed for these models. The strain energy per atom (under zero external stress) is defined by the general expression

$$e / v = \tfrac{1}{2} \sum c_{ijkl} \epsilon_{ij} \epsilon_{kl} , \tag{4}$$

where v is the atomic volume, ϵ_{ij} represents the infinitesimal strain and where we have used the full tensor notation. The strains associated with these stresses are most conveniently obtained through stress-strain relations involving the elastic compliances, which are ap-

proximated to obey the isotropy relations since it is of interest to obtain only a rough estimate of the strain energies. In Table III we present values of isotropic elastic moduli, λ and μ, and corresponding strain energies associated with our models. The "isotropic" elastic constants are derived from Table II, where appropriate averages are taken. [For μ, both elastic-constant types c_{44} and $(c_{11} - c_{12})/2$ are averaged together.] Additionally, in the case of model III, a conversion[23] from the C_{ij}'s of Table II to the ordinary elastic constants was made within the approximation that only isotropic stress, with a value corresponding to the virial pressure of model III, is present. It should also be noted that, by employing expression (4) and the values in Table III, we are making the tacit assumption that there is a negligible difference in the second-order elastic constants between a zero-stress state and that corresponding to the stresses of Table I. Further, the values of the strain energy are larger than the kinetic energy of the final iteration in the relaxation procedure by factors ranging from 4 to 100 for the 216-atom models considered. Thus, whereas additional relaxation of some of our 216-atom models is possible, the uniformity of the results for the strain energies suggest that these values are intrinsic to the algorithms used—given the SW potential, 216-atoms, and cubic periodic boundary conditions. In the case of model V, the strain energy is seen to be an order of magnitude smaller than for the 216-atom models and it is larger than the kinetic energy of the final relaxational iteration by a factor of 10^4.

V. COMPARISON OF ELASTIC MODULI WITH EXPERIMENT AND EARLY MODEL CALCULATIONS

It is also worthwhile to present experimentally extracted values of the elastic constants as well as results based on a "scaling" of the theoretical results of Steinhardt et al.[6] for a-Ge. Tan et al.[1] determined the room-temperature value of Young's modulus, E, to be 12.4 ± 0.3, which, when combined with the measured Rayleigh surface-wave velocity of Senn et al.[2] of 4.16×10^5 cm/s, yields $\lambda = 58.7^{+90}_{-40}$ and $\mu = 4.23^{+0.07}_{-0.02}$ where elastic moduli are in units of 10^{11} dyn/cm^2. Similarly, if the measured room-temperature, surface-wave velocity of Vacher et al.[3] of 4.29×10^5 cm/s is used instead, we obtain $\lambda = 8.33^{+5.7}_{-3.0}$ and $\mu = 4.70 \pm 0.1$. (In this work we adopt the value 2.21 g/cm^3 for the experimental

density of a-Si.[7]) These results are based on the standard flat-surface analysis of the Rayleigh surface-wave velocity in terms of elastic constants of an isotropic medium; for the former set of elastic constants, the full variation in E could not be reflected in the uncertainties in λ and μ since above $E=12.5$ there are no solutions to the Rayleigh equation. Clearly the latter set of results is most consistent with the values in Table III. In addition, the former set of results leads to unreasonably large values of the bulk modulus. In view of the fact that values of the density, as well as of the coordination, of crystalline and amorphous Si are quite similar, we expect the bulk moduli to be similar between the two structures as well. This is the case for the latter set of experimental values, which yields $B=11.5^{+5.6}_{-3.0}$ to be compared with the crystalline value of 9.8. However, the former set yields values of the bulk modulus in excess of 21.7, which are unreasonably high in our opinion. In order to indicate the effect of a possible uncertainty in the density, a density of 2.23 g/cm^3 yields $\lambda=7.14$ (34.4) and $\mu=4.77$ (4.29) for the results of Vacher et al. (Senn et al.), i.e., to be compared with the corresponding above results, $\lambda=8.33$ (58.7) and $\mu=4.70$ (4.23). It must also be noted that Vacher et al.[3] did not state the density of their amorphized sample.

Guttman's[4] calculational results for elastic moduli of amorphous models were presented in terms of α/r, where r is the near-neighbor distance in the corresponding crystalline material. Kluge and Ray[7] applied Guttman's results to the case of a-Si by fitting the Keating expression to the experimental result for c_{11}; their results correspond to $\lambda=5.2$ and $\mu=6.05$. Steinhardt et al.[6] assumed a Keating-like potential, but with a value $\beta/\alpha=0.2$, whereas Guttman's values are based on the Keating potential with a value of $\beta/\alpha=0.3$, quite close to the Keating value. Since Steinhardt et al.[6] presented results for a-Ge, it is necessary to scale their results to a-Si. This is done through the parameter α/r. We obtain α from (a) the two-body part of the SW potential (α is equivalent to "F" of Ref. 10), and (b) a fit of the Keating expression for c_{11} to experiment, or $c_{11}=1.2\alpha/r=16.6$, where we set $\beta/\alpha=0.2$ in the Keating expression. We obtain λ (μ) to be 6.75 (5.63) and 6.90 (5.76) for cases (a) and (b), respectively. Steinhardt et al.[6] also presented results for the effect of "relaxation" on the elastic constants, as the elastic constants can be written as the sum of two terms, one which corresponds to an affine deformation—and which alone is present when each atom is a center of symmetry—and one which allows for variation of the atomic coordinates in the presence of a macroscopic strain. In the calculation of Steinhardt et al.,[6] the boundary-atom displacements were determined by an affine deformation. In Table IV we compare our shear and bulk moduli results with those in Ref. 6. The unrelaxed elastic constants do not obey the isotropy conditions very well only in the case of model I; $\langle c_{44}\rangle=8.21$ and $(\frac{1}{2})(\langle c_{11}\rangle-\langle c_{12}\rangle)=5.84$, where $\langle\ \rangle$ indicates averages over cubic-symmetry-equivalent indices. Therefore, Voight polycrystalline averages are included (values in parentheses) for model-I entries in Table IV. Our models clearly yield larger relaxational effects than those of Ref. 6, and we note that a large relaxational

effect in μ may be generally characteristic of amorphous materials as it appears to be present in amorphous metals as well.[25]

VI. APPLICATION TO PRESSURE DEPENDENCIES AND DEBYE TEMPERATURES

Here we apply the above results to obtain estimates of the Debye temperature, Grüneisen parameter, and the pressure derivatives of elastic constants. The pressure derivatives of elastic constants can be estimated by comparing results for models III and IV since these models differ primarily through the difference, 4.078 GPa, in their virial pressures. Thus we obtain $\lambda'=5.5$ and $\mu'=0.25$ (the primes denote d/dp). Because of the close relationship between models IV and V, slightly more reliable results might be obtained by replacing the λ and μ values of model IV by those of model V. This yields $\lambda'=4.5$ and $\mu'=0.27$. Next we compare SW static-lattice results with experiment for the case of crystalline Si: The calculated (experimental)[26] values are 2.97 (4.29), 2.75 (4.20), and 0.183 (0.75), for c'_{11}, c'_{12}, and c'_{44}, respectively, where the experimental values correspond to $T=77.2$ K. We note that the large underestimate of c'_{ij} by the SW potential is not surprising since a previous MD result[16] showed that the SW potential similarly underestimates the high-temperature value of the thermal expansivity.

The Debye temperature Θ_0 (based on our isotropic elastic constants) of each model is given in Table III. In Table V we compare SW results with the corresponding experimental crystalline[27–29] and amorphous[30] values for the quantities Θ_0 and γ_0, where γ_0 is the thermodynamic Grüneisen parameter ($T=0$ K limit). The quoted uncertainty of the SW value of Θ_0 is based on the maximum deviation of results for models I, II, and IV from their average value. In addition, the Grüneisen parameter is estimated from results for Θ_0 of models III and IV and is found to have a rather small magnitude, not unlike the case of the crystal that has negative thermal expansion at not overly low temperatures.[29] Furthermore, from the

TABLE IV. Relaxation effects in bulk and shear moduli: R, relaxed; U, unrelaxed (in units of 10^{11} dyn/cm^2).

		B	μ
Steinhardt et al.[a]	R	10.50	5.63
	U	10.76	8.94
Model I	R	10.31 (10.17)	3.26 (3.31)
	U	13.92 (13.13)	7.03 (7.27)
Model II	R	10.13	3.36
	U	12.01	7.15
Model III	R	10.84	3.12
	U	13.18	7.54
Model IV	R	8.52	3.01
	U	11.09	6.96
Model V	R	8.98	3.00
	U	10.84	6.91

[a]Based on scaling choice (a) (see text) of values in Ref. 6.

TABLE V. Low-temperature Debye temperatures and Grüneisen parameters.

| | Θ_0 (K) | | γ_0 | |
	Amorphous	Crystalline	Amorphous	Crystalline
SW[a]	460 ± 13	554.2	-0.1[g]	0.4
Expt. (thermal)	528 ± 20[b]	645 ± 5[e]		0.44[h]
Expt. (elastic)[a]	538 ± 1[c]	650[f]		0.25[i]
	557 ± 1[d]			0.21[h]

[a]de Launay's tables were used to compute "crystalline" values of Θ_0.

[b]Reference 30.

[c]Based on (room-temperature) results of Refs. 1 and 2 and standard formula, in terms of λ and μ, for the Rayleigh surface-wave velocity on a flat surface. Uncertainty reflects quoted uncertainty in Young's modulus alone (see text).

[d]Based on (room-temperature) results of Refs. 1 and 3 (see footnote c).

[e]Reference 27.

[f]Based on $T=77.2$ K elastic-constant values given in Ref. 26.

[g]We do not know how to estimate the uncertainty (see text).

[h]Reference 29.

[i]Reference 28.

values of Θ_0, in Table IV, our models are seen to accurately yield the increase, due to amorphization, in the low-temperature aT^3 term in the specific heat: We find $a_{\text{cryst}}/a_{\text{amor}}=0.57\pm8\%$ ($0.55\pm15\%$) in the case of the SW potential (experiment). On the other hand, it is seen that the absolute value of Θ_0 given by theory is in error.

We also present (Table V) a comparison of the measured[30] heat-capacity and experimentally determined elastic-constant Θ_0 values for a-Si. These results are inconclusive vis à vis the existence of an "extra" contribution to the T^3 heat capacity, known to occur for many glasses.[31] If an extra contribution existed, we would have found an elastic-constant value larger than the calorimetric one, and only one of the two "measurements" for the elastic-constant value is outside the range of possible calorimetric values. It should also be recalled that a large linear heat-capacity term at very low temperatures is also characteristic of insulating glasses and generally ascribed to two-level tunneling systems. Such a term was not observed in the heat capacity of a-Ge, although careful measurements on that material have been made below 1 K.[32] (We are not aware of measurements performed at sufficiently low temperatures to rule out such a term in the heat capacity of a-Si.)

Returning to our quoted result (Table V) for γ_0, the possibility that γ_0 is negative is intriguing since that would imply that the thermal expansivity is predicted to be negative in the $T=0$ K limit. It might appear that there is a substantial uncertainty in this result, indicated by the deviations from isotropic conditions, i.e., the values in parentheses in Table III. Indeed, if we had chosen appropriate individual elastic-constant values rather than averaged values, a large positive value of γ_0 could have been obtained. However, we believe that such considerations greatly overestimate the uncertainty in γ_0 since some "self-averaging" of elastic constants most likely occurs in going to larger models, as indicated by the closeness in values of Θ_0 for models IV and V.

VII. CONCLUSIONS

We demonstrated the use of the method of long waves for evaluating elastic constants of four different 216-atom models as well as a 1000-atom model of amorphous Si. An important feature of these models in applying the method is that they have periodic boundary conditions. Our results were found to be consistent with previous related theoretical estimates of elastic constants at finite temperatures. Unfortunately, combined uncertainties preclude obtaining reliable differences between our static-lattice values and the high-temperature values of Kluge and Ray for the purpose of estimating temperature dependencies. On the other hand, rough estimates of pressure effects were possible. External stresses based on the Born-Huang conditions were also obtained. These quantities were found to be ≤ 0.9 GPa for the 216-atom models and ≤ 0.3 GPa for the 1000-atom model. It seems worth pointing out that those stresses are comparable to the value 0.2 GPa, which represents the measured[1] internal-stress component for a thin-film a-Si sample made by ion implantation.

Finally, we have given detailed information pertaining to the energetics of these models. We found that the 1000-atom model was lower in potential energy than its closely related 216-atom model (model IV) by 3×10^{-3}, whereas the strain energy in the 216-atom model was found to be merely 5.6×10^{-4} (in SW units/atom). Thus the difference in energies between the two models does not primarily represent a relaxation of internal stresses in the larger model, although such a relaxation clearly takes place on the basis of our results.

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