Evaluation of Gruneisen parameters, third-order elastic constants, and other associated properties of amorphous As

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Pressure derivatives of second-order elastic constants of amorphous As have been derived through the use of Schofield's equations and Bhatia-Singh's (BS) parameters. By using these equations the longitudinal and transverse Gruneisen parameters, which are related to third-order elastic constants (TOEC), have been calculated. A method has been described to evaluate the third-order elastic constants. Shiren's nonlinear parameter has been used to calculate the third-order elastic constant C_{155} which is found to be in satisfactory agreement with experiment. Nath-Smith–DeLaunay's equation has been used to compute the position of the absorption band and this is compared with that obtained from BS parameters. There is good agreement between the two values. The $\gamma_g^{\rm el}$ calculated from Nath-Smith–DeLaunay's equation gives good result in agreement with that calculated from γ_g^L and γ_g^T, which are obtained from Schofield's and BS equations. Phonon frequencies have been evaluated through the BS method. It is found that in the case of $\omega_L(k)$ the collective nature of excitons persists up to large wave vector **k**.

I. INTRODUCTION

Precise experimental data is necessary in the study of vibrational properties of solids in the long-wavelength limit. The complete sets of tensor components for an amorphous substance such as *a*-As have been determined by Brassington and co-workers.[1,2] It is an important technological material.[3] A model of *a*-As reviewed by Greaves, Elliot, and Davis[3] envisages that *a*-As is more open than in crystalline form and proposes a possible double-layer configuration in which the double layers buckle beyond a few bond lengths. The third-order elastic constants (TOEC's) are of interest because they characterize the anharmonic properties, that is the nonlinearity of the atomic forces with respect to atomic displacements and throw light on the phonon-phonon interactions.[4] We have evaluated the longitudinal γ_g^L and transverse γ_g^T Gruneisen parameters through the use of experimental pressure derivatives.[1] There are two reasons for this calculation. One reason is that both γ_g^L and γ_g^T are related to the TOEC's. The second reason is to verify the recently derived equations by the authors[5,6] in the evaluation of these parameters and hence verify their applicability.

Using experimental second-order elastic constants (SOEC's) we obtain Bhatia-Singh's (BS) parameters to evaluate the phonon frequencies.[7] In addition we predict the absorption band position of *a*-As both through the use of SOEC's and BS parameters. Finally we use the compressibility equation of state and obtain a value for the packing fraction $\eta=\pi\rho\sigma^3/6$ which may be thought of as an effective packing fraction. Here ρ is the number density and σ is the hard-sphere diameter. Using this value we calculate other properties of *a*-As.

II. THEORY

Starting with Schofield's equations[8] for SOEC's it can be shown[5]

$$\frac{dC_{11}}{dP}=C_{11}\chi_T+1.8(C_1^L-1), \tag{1}$$

$$\frac{dC_{44}}{dP}=C_{44}\chi_T+0.6(C_1^T-1). \tag{2}$$

Here χ_T is the isothermal compressibility. Here

$$C_1^{L,T}=2\gamma_g^{L,T}+1/3. \tag{3}$$

This equation is in conformity with the general equation derived by Debye,[9] namely

$$C_1=\frac{dB}{dP}=\frac{d}{dP}\left(\frac{1}{\chi_T}\right)=2\gamma_g^{\rm th}+\frac{1}{3}. \tag{4}$$

Here $\gamma_g^{\rm th}$ is the thermal Gruneisen parameter and B is the bulk modulus. Hence from Eqs. (1) to (3) it is possible to evaluate γ_g^L and γ_g^T, the longitudinal and transverse Gruneisen parameters, and these are related to TOEC's.[10] The bulk modulus changes with pressure and causes frequency changes both longitudinally and transversely and hence we evaluate γ_g^L from dC_{11}/dP and γ_g^T from dC_{44}/dP. It is also possible to evaluate γ_g^L and γ_g^T from BS parameters. We have according to BS theory[7]

$$C_{11}=n_c[(1/3)\beta+(1/5)\delta]+k_e, \tag{5}$$

$$C_{44}=n_c[(1/3)\beta+(1/15)\delta]. \tag{6}$$

Here, K_e is the electronic bulk modulus

$$\beta=\frac{\rho_w a^2}{2M}\left(\frac{1}{r}\frac{d\phi}{dr}\right)_{r=a}, \tag{7}$$

$$\delta=\frac{\rho_w a^3}{2M}\left[\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)\right]_{r=a}. \tag{8}$$

n_c is the number of nearest neighbors, ϕ is the potential function, a is the nearest-neighbor distance, M is the mass of the particle, and ρ_w is the weight density. We differentiate Eq. (5) with respect to pressure and neglect (dK_e/dP) in comparison to the first term in Eq. (5). We obtain, after doing some algebra[6]

$$\frac{dC_{11}}{dP}=\chi_T n_c\left[\frac{1}{45}\,(\delta+5\beta)+\frac{2}{5}\,\gamma_g^L(\beta+\delta)\right]. \tag{9}$$

Similarly one can obtain (dC_{44}/dP) and the result is

$$\frac{dC_{44}}{dP}=\chi_T n_c\left[\frac{1}{9}\left(\beta-\frac{3}{5}\,\delta\right)+\frac{2}{15}\,\gamma_g^T(\beta+\delta)\right]. \tag{10}$$

A. Method of evaluation of TOEC

It was shown earlier that C_{111} is related to the SOEC (Ref. 11) as

$$\frac{C_{111}}{C_{11}}=-[5+\chi_T C_{11}(C_1-1)], \tag{11}$$

$$C_1\equiv\frac{dB}{dP}\equiv\frac{d}{dP}\left(\frac{1}{\chi_T}\right) \tag{12}$$

C_1 is related to TOEC's through the Birch equation.[12] Using the experimental values of C_{11} and C_1 we can calculate C_{111}.

Further we have Thurston's relations[13]

$$C'_{11}=(dC_{11}/dP)=-(1/3)\chi_T(C_{111}+2C_{112}), \tag{13}$$

$$C'_{44}=(dC_{44}/dP)=-(1/3)\chi_T(C_{144}+2C_{116}), \tag{14}$$

$$C'_{12}=-(1/3)\chi_T(2C_{112}+C_{123}). \tag{15}$$

We assumed for isotropic a-As, $C_{113}=C_{112}$ and $C_{155}=C_{166}$ in the above equations. The Birch equation can be written in Brugger's notation as,[1]

$$C_1=\frac{-\chi_T}{9}\,(C_{111}+6C_{112}+2C_{123}). \tag{16}$$

From Eqs. (11), (13), and (16) we can evaluate C_{111}, C_{112}, and C_{123}. Pomerantz quoted[14] that Shiren, while investigating the attenuation of longitudinal phonons, has derived an equation which contains a nonlinear constant K for the $\langle 100\rangle$ and $\langle 110\rangle$ directions in cubic systems which are isotropic. For isotropic a-As, K is connected to the TOEC by

$$K=3+(C_{111}/C_{11}) \quad \text{for } \langle 100\rangle, \tag{17}$$

$$K=3+[(1/2)C_{111}+(3/2)C_{112}+6C_{155}]/\alpha \quad \text{for } \langle 110\rangle, \tag{18}$$

where

$$\alpha=C_{11}+C_{12}+2C_{44}. \tag{19}$$

Since we are dealing with a-As we assume that both Eqs. (17) and (18) are valid as we can fix no particular direction for an amorphous substance. We evaluate K from Eq. (17), and calculate C_{155} from Eq. (18). Then from Eq. (11) we obtain C_{144}. As shown earlier by Brassington *et al.*,[1]

$$C_{155}=C_{144}+2C_{456}, \tag{20}$$

from which we get C_{456}. This completes the method of evaluation of the TOEC. At this stage it may be mentioned that for an isotropic substance only three TOEC's are independent. These can be chosen as C_{123}, C_{144}, and C_{456} and the remainder are given by linear combinations of these three.[1]

B. Calculation of absorption band position in a-As through elastic constants and Bhatia-Singh's parameters

It was shown by Nath-Smith and by De Launay[15] that

$$\frac{8A(A+8C_{11}-16C_{44})}{[3A-8C_{11}+16C_{12}]^2}=1, \tag{21}$$

where

$$A=\omega^2 M/2a. \tag{22}$$

Here ω is the frequency of absorption, M is the mass of the material particle from which we can calculate ω and hence the position of the absorption band.

To use the BS parameters to evaluate ω we proceed as follows. We define an anisotropy parameter S as

$$S=\frac{2C_{44}}{C_{11}-C_{12}}. \tag{23}$$

Using BS equations[7] for C_{11} and C_{44} [viz. Eqs. (5) and (6)] and from Eqs. (21) and (22) we get

$$(\alpha_1/\alpha_2)=1, \tag{24}$$

where

$$\alpha_1=8A\left[A+8\left(\frac{1}{15}\,n_c\delta-\frac{n_c\beta}{3}+k_e\right)\right], \tag{25}$$

$$\alpha_2=\left[3A+8\left\{\frac{1}{3}\,\beta(n_c-4n'_c)+\frac{1}{15}\,\delta(3n_c-4n'_c)+k_e\right\}\right]^2. \tag{26}$$

Here

$$n'_c=n_c/S. \tag{27}$$

Since for the isotropic substance $S=1$, Eq. (25) simplifies to

$$\alpha_2=\left[3A-8\left\{\beta n_c+\frac{1}{15}\,\delta n_c-k_e\right\}\right]^2. \tag{28}$$

k_e, the electronic bulk modulus, has been calculated using Sommerfield's theory[15] and has been amply described in several of our papers[16,17] and hence the method of calculation will not be repeated here. Thus knowing k_e, β, δ, and n_c one can calculate A from Eqs. (24), (25), and (28). Equations (19)–(26) assume importance when β and δ are determined by an independent method, for instance, directly from the potential function generated by the molecular-dynamics method.

TABLE I. Calculated values and literature data (Ref. 1) used for phonon frequencies.

Wigner-Seitz radius=	1.84 Å
Thomas-Fermi inverse screening length=	2.11×10^{8} cm^{-1}
k_f=	1.84 Å^{-1} (Ref. 25)
n_c=	3 (Ref. 25)
B=	17.5 GPa (Ref. 1)
β=	−0.31 GPa
δ=	+47.92 GPa
K_e=	+1.35 GPa
C_{11}=	29.8 GPa (Ref. 1)
C_{12}=	11.3 GPa (Ref. 1)
C_{44}=	9.274 GPa (Ref. 1)
ρ_w=	4.77 gm/cm^3

C. Evaluation of phonon frequencies through BS method (Ref. 7)

According to Bhatia and Singh, the longitudinal and transverse phonon frequencies are given by

$$\rho_w\omega_L^2(k)=\frac{2n_c}{a^2}\,(\beta I_0+\delta I_2)+\frac{k_eK_{\rm TF}^2[G(kr_s)]^2k^2}{k^2+K_{\rm TF}^2\tilde{g}(k)}, \tag{29}$$

$$\rho_w\omega_T^2(k)=\frac{2n_c}{a^2}\,[\beta I_0+0.5\delta\,(I_0-I_2)]. \tag{30}$$

Here $K_{\rm TF}$ is the Thomas-Fermi screening length, $G(kr_s)$ is the shape factor, r_s is the Wigner-Seitz radius, $\tilde{g}(k)$ is the Linhard-Langer-Vosko function,[18] and I_0 and I_2 are functions of k. The expressions for $G(kr_s)$, $\tilde{g}(k)$, I_0, and I_2 are already given in various papers[7,16,17] and will not be repeated here. We would like to state that the values of the phonon frequencies do not depend critically on the value of k_e[7]. In fact, Bhatia-Singh treat k_e as a parameter.

D. Evaluation of elastic Gruneisen parameter

The elastic Gruneisen parameter is generally defined as[1]

$$\gamma_g^{\rm el}=\frac{1}{3}\,[\gamma_g^L+2\gamma_g^T]. \tag{31}$$

This equation is true at high enough temperatures when all the vibrational modes are excited.[1] We now give a method for the evaluation of $\gamma_g^{\rm el}$. Differentiating Eq. (21) and with pressure we obtain for isotropic a-As (for which $S=1$)

TABLE III. Absorption band position.

From Bhatia-Singh's parameters	355.6 cm^{-1}
From Nath-Smith–DeLaunay equation	347.5 cm^{-1}

$$\frac{dA}{dP}=\left[8\left(\frac{dC_{11}}{dP}\right)(3A-8C_{11}+16C_{12})+16\left(\frac{dC_{12}}{dP}\right)\times(8C_{11}-16C_{12}-A)\right](A-24C_{11}+16C_{12})^{-1}. \tag{32}$$

From Eq. (22) we get

$$\frac{dA}{dP}=\beta_TA[2\gamma_g^{\rm el}+(1/3)]. \tag{33}$$

Here we assumed along with others[19] that for a-As, $V\alpha r^3$. From Eqs. (32) and (33) we can easily calculate $\gamma_g^{\rm el}$. In many cases the structure factor of amorphous substances and liquids show a great resemblance.[20–22] Hence it is interesting to see how the liquid-state equation is applicable to amorphous solids. We have the relation connecting compressibility and packing fraction for hard-sphere liquids as[23]

$$\frac{B}{Pk_BT}=\frac{(1+2\eta)^2}{(1-\eta)^4}=\frac{1}{S(0)}. \tag{34}$$

Using the experimental value of χ_T, we obtain a value of 0.57 for η which we consider as the effective packing fraction and calculate C_1. We obtain from Eq. (34)

$$C_1=1+\frac{4S(0)\,\eta(1+2\eta)(2+\eta)}{(1-\eta)^5}, \tag{35}$$

where

$$S(0)=\rho k_BT\beta_T. \tag{36}$$

From Eqs. (35) and (36) we can calculate C_1.

III. RESULTS

The input data are taken from Ref. 1. The calculated values of the parameters β, δ, K_e, etc. are given in Table I. The phonon frequencies have been calculated through the BS method.[7,16] The calculated longitudinal (γ_g^L) and transverse (γ_g^T) Gruneisen parameters calculated by different methods and $\gamma_g^{\rm el}$ are given in Table II.

The absorption band positions calculated by different methods are given in Table III. Unfortunately there are no experimental results to compare with. The calculated values

TABLE II. Longitudinal and transverse Gruneisen parameters through Schofield's and the BS methods.

γ_g^L			γ_g^T		
BS	Sch.	Expt. (Ref. 1)	BS	Sch.	Expt. (Ref. 1)
2.39	2.10	2.35	2.00	1.34	1.45

$\gamma_g^{\rm el}$ evaluated from Nath-Smith–DeLaunay equations and from γ_g^L and γ_g^T

From Eq. (28) and (29)	From $\gamma_g^{\rm el}=(1/3)(\gamma_g^L+2\gamma_g^T)$
1.82	1.74 (Ref. 1)

TABLE IV. Third-order elastic constants in GPa.

	Theory	Expt. (Ref. 1)
C_{123}	−176	−162
C_{144}	+91	+68
C_{456}	−91	−86

of three independent TOEC's are given in Table IV as a-As is isotropic.

IV. DISCUSSION

Both $\omega_L(k)$ and $\omega_T(k)$ show a linear rise at low values. However $\omega_L(k)$ soon attains a maximum at $k=1.6$ Å^{-1} and oscillates giving rise to two peaks at $k=4.2$ Å^{-1} and at $k=6.8$ Å^{-1}. This shows that in a-As the collective nature of excitons persist up to large k. In this connection it is worth mentioning that the structure factor of liquid As is quite complex[24,25] and shows three distinct peaks. Assuming that this is also true in a-As, we feel that the oscillations in $\omega_L(k)$ as shown in Fig. 1 are in accord with the collective nature of $\omega_L(k)$. $\omega_T(k)$ reaches a maximum and remains almost constant.

From Table I we observe that the electronic bulk modulus in the semimetal a-As is about 11% of the bulk modulus which is 17.4 GPa.[1] From Table II we see that γ_g^L calculated through the BS method and Schofield's equation are in very good agreement with experiment. However in the case of γ_g^T the BS equation gives a high value, while the one obtained from Schofield's method is in good agreement with experiment. It appears that Schofield's equations though simple and meant for liquids give very good results in agreement with literature values.[1] The $\gamma_g^{\rm el}$ calculated from Nath-Smith and De Launay's equation[15] [viz. Eqs. (32) and (33)] is in good agreement with that obtained from γ_g^L and γ_g^T [viz. Eq. (31)].

The band absorption position (viz. Table III) as obtained by both the methods are in very good agreement. However there is no experimental data to compare with the theoretical values. From Table IV we observe with satisfaction that the TOEC's calculated and observed are in good agreement with experiment[1] except for C_{144}. Even in this case the agreement

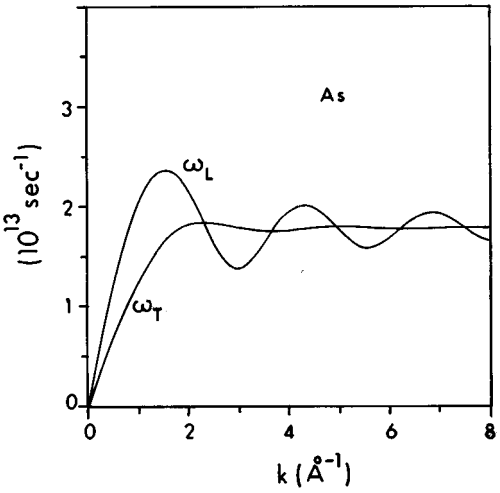

FIG. 1. Longitudinal and transverse phonon frequencies versus k.

with experiment[1] is reasonable. It is gratifying to note that this simple theory accounts well in producing γ_g^L and γ_g^T, as well as the TOEC's. It is noted that the nonlinear constant K gives a value of −94 GPa for C_{155}, while that given by Brassington *et al.*[1] is −108 GPa. The value obtained for C_1 from Eq. (35) is 7.4 with $\eta=0.58$. This compares favorably with the experimental value of 6.4.[1] It may be pointed out that Eq. (35) is sensitive to η. Thus the present treatment using Schofield's and BS theories yields γ_g^L, γ_g^T and TOEC's in satisfactory agreement with experiment,[1] while the pressure derivative of Nath-Smith–De Launay's equation gives a very good value for $\gamma_g^{\rm el}$ in agreement with experiment and a fair value of C_1.

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[1] M. P. Brassington, W. A. Lambson, A. J. Miller, G. A. Saunders, and Y. K. Yogurteu, Philos. Mag. B **42**, 127 (1980).
[2] M. P. Brassington, A. J. Miller, and A. J. Saunders, Philos. Mag. B **43**, 1049 (1981).
[3] G. N. Greaves, S. R. Elliot, and E. A. Davis, Adv. Phys. **28**, 49 (1979).
[4] L. H. Taylor and F. R. Rollins, Phys. Rev. A **133**, 591 (1964).
[5] R. V. Gopala Rao and R. Venkatesh, J. Non-Cryst. Solids **175**, 278 (1994).
[6] R. V. Gopala Rao and R. Venkatesh, Pramana **42**, 201 (1994).
[7] A. B. Bhatia and R. N. Singh, Phys. Rev. **31**, 475 (1985).
[8] P. Schofield, Proc. Phys. Soc. London **88**, 149 (1966).
[9] S. E. Babb, Jr., J. Chem. Phys. **38**, 2743 (1963).
[10] K. Brugger and T. C. Fritz, Phys. Rev. **157**, 524 (1967).
[11] R. V. Gopala Rao and R. Venkatesh, Phys. Rev. B **39**, 9467 (1989).
[12] F. Birch, Phys. Rev. **71**, 809 (1947).
[13] R. N. Thurston, Proc. IEEE **53**, 132 (1965).
[14] M. Pomerantz, Phys. Rev. **139A**, 501 (1965).
[15] J. De Launay, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2, p. 296; H. B. Huntington, *ibid*. Vol. 7, p. 301.
[16] R. V. Gopala Rao and R. Venkatesh, Physica B **190**, 417 (1993).
[17] R. V. Gopala Rao and R. Venkatesh, Phys. Status Solidi B **176**, 317 (1993).

[18] S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1959).
[19] D. Gerlich, E. Litov, and G. L. Anderson, Phys. Rev. B **20**, 2529 (1979).
[20] O. Vemura, Y. Sagara, D. Muno, and T. Satow, J. Non-Cryst. Solids **30**, 155 (1978).
[21] O. Vemura, Y. Sagara, M. Tsushima, T. Kamikawa, and T. Satow, J. Non-Cryst. Solids **33**, 71 (1979).
[22] T. Satow, O. Vemura, and S. Akaike, J. Non-Cryst. Solids **29**, 215 (1978).
[23] C. A. Croxton, *Introduction to Liquid State Physics* (Wiley, New York, 1975), p. 86.
[24] R. Bellisent, C. Bergman, R. Ceolin, and J. P. Gaspard, Phys. Rev. Lett. **59**, 661 (1987).
[25] J. Hafner, Phys. Rev. Lett. **62**, 784 (1989).