

Vibrational excitations in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys

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We report here the results of a first calculation of the vibrational excitations of hydrogenated $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys using a cluster-Bethe-lattice method. The study has been made for two types of distributions of constituent atoms of the alloy: a random sequence and a chemically ordered one. The infrared data of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys can be well understood if one assumes the occurrence of a random distribution of Si and C atoms. The vibrational modes induced by H atoms outside the bulk phonon region of an $a\text{-Si}_{1-x}\text{C}_x$ alloy remain undisturbed by the presence of the kind of atoms lying on the next-nearest-neighboring sites of the H atom. On the other hand, the frequencies of modes induced by H atoms lying in the bulk phonon region change regularly due to the presence of the different concentrations of the Si and C atoms in the alloy. The calculated results are in good agreement with the available infrared data. However, more careful and detailed experimental investigations are very much needed to detect the predicted extra structure, especially in the bulk phonon-frequency region.

I. INTRODUCTION

Improvement in the conversion efficiency is the most important point for the practical application of the $a\text{-Si}$ solar cell as an alternate nonconventional source of energy. A conversion efficiency of 11–12% has recently been reached in Si-based devices in textured structures.¹ In an attempt to attain much higher conversion efficiency, multiple-band-gap $a\text{-Si}$ solar cells have to be developed. This stems from the fact that, in contrast to the theoretical limit of maximum efficiency of 12.5–13% for the conventional single-band-gap $a\text{-Si}$ solar cell, multiple-band-gap $a\text{-Si}$ solar cells named tandem solar cells may have an estimated value of 21–24%.²

Amorphous hydrogenated silicon carbon alloys have an energy gap larger than that of $a\text{-Si:H}$ or $a\text{-Si:F,H}$. They have potential applications in tandem solar cells and also in electrophotography. Some experimental investigations have so far been reported in the literature.^{3–10}

In contrast to the many experimental investigations, virtually no theoretical attempt has been made to understand the behavior of the hydrogenated or fluorinated semiconducting alloys. In particular, no result of any serious investigation of the hydrogenated or fluorinated amorphous $\text{Si}_{1-x}\text{Ge}_x$, $\text{Si}_{1-x}\text{C}_x$, or $\text{Si}_{1-x}\text{N}_x$ alloy has so far been reported. Our group is presently engaged in a detailed theoretical study of the vibrational and electronic excitations of these semiconducting alloys containing H, F, O, etc.

Earlier, we reported the results of our study of the vibrational excitations of $a\text{-Si}_3\text{N}_4\text{:H}$,¹¹ $a\text{-Si}_{1-x}\text{Ge}_x\text{:F,H}$, and $a\text{-Ga}_{1-x}\text{Al}_x\text{As}$ alloys.¹² The electronic structure of $a\text{-Si}_{1-x}\text{Ge}_x\text{:F,H}$ alloys has also been discussed.¹³ The phonons of a perfect silicon carbide network containing monohydrides, dihydrides, and trihydrides have been investigated.¹⁴ The present paper is the third of a series of our reports on these materials.

A cluster-Bethe-lattice method (CBLM) is particularly suited for the study of short-range order or disorder. The usefulness of the method arises from the fact that the properties of small regions of atoms can be isolated. Here, the problem is exactly solvable in contrast to the difficulties faced in other methods.

In the present paper, we report the results of our investigations of the phonons of the hydrogenated amorphous $\text{Si}_{1-x}\text{C}_x\text{:H}$ alloys. For the details of the CBLM and the different types of occurrence of the atomic configurations, we refer to our earlier papers.^{11–14}

II. CALCULATIONS AND RESULTS

A. $a\text{-SiC}$: Bulk phonons

The phonons for the bulk amorphous silicon carbide network (Bethe lattice) were calculated by employing a value of radial force constant $\alpha(\text{Si-C})$ which reproduces the high-frequency transverse-optic (TO)-like peak at 781 cm^{-1} , in agreement with the experiment data.¹⁵ The non-central force constant in the Born model was scaled by using the force constant obtained for the pure $a\text{-Si}$ alloys. These force constants are shown in Table I. Then the corresponding force constants for the C—C bonds were determined by making the assumption that the values of the force constants for the Si—C bonds should be the mean of the corresponding values for the Si—Si and C—C bonds.

The low-frequency phonons arise mainly from the Si—Si bonds of the heavy Si atoms, whereas the high-frequency vibrations originate from the C—C bonds of the low-mass C atoms. For pure $a\text{-Si}$, the high-frequency (transverse-optic-like) peak and the transverse-acoustic-like low-frequency peak appear at 480 and 195 cm^{-1} , respectively. The corresponding values for $a\text{-C}$ in the tetrahedral network are 1079 and 425 cm^{-1} , respectively.

TABLE I. Values of the force constants used for various configurations (in units of 10^4 dyn/cm). Angle-bending force constant $K(\text{C—Si—C})=K(\text{Si—C—Si})=0.60$; radial force constant $\alpha(\text{Si—C})=18.5$; angular force constant $\beta(\text{Si—C})=3.0$. Bond lengths used are $d(\text{Si—C})=1.89$ Å, $d(\text{Si—H})=1.48$ Å, and $d(\text{C—H})=1.07$ Å.

Unit	Force constants		
	Radial	Angle bending	
	$\alpha(\text{Si—H})$	$K_1(\text{C—Si—H})$	$K_3(\text{H—Si—H})$
SiH	25.04	1.074	
SiH ₂	25.04	1.074	1.92
SiH ₃	25.04	1.074	1.92
	$\alpha(\text{C—H})$	$K_1(\text{Si—C—H})$	$K_3(\text{H—C—H})$
CH	46.30	1.86	
CH ₂	46.30	1.86	4.20
CH ₃	46.30	1.86	4.20

B. α -Si_{1-x}C_x alloys

The local phonon density of states at both the C and Si atoms has been calculated for the entire concentration range ($0.01 < x < 0.99$) both for the random and chemically ordered sequences. The results for the two sequences are shown in Figs. 1 and 2, respectively. For the sake of comparison, the results for bulk Si and C matrices are also included. In

the random configuration of atoms for low concentration x of the C atoms in the silicon matrix, a localized peak arising from the motion of a carbon atom sitting in the cage of Si atoms appears at 750 cm^{-1} . The frequency of the other strong peak arising from Si-Si TO-like modes decreases with an increase in x . For large values of x , the light C atom-induced localized modes start interacting among themselves and the sharp peak originating from the isolated C atom gets broadened with an increase of the C atoms, eventually merging with the low-frequency Si—Si bond bulk modes. For $x > 0.8$, the number of C—C bonds dominates and the phonon density resembles that of bulk α -C. However, there appears a resonance mode at 300 cm^{-1} originating from the heavy Si atom in the cage of light C atoms.

In the chemically ordered configurations of atoms, where an atom in minority concentration is coupled always to the atoms in majority as nearest neighbors, the results are slightly different. The interaction between the localized modes at $\sim 750\text{ cm}^{-1}$ originating from C atoms is weaker than that seen earlier in the random network. As a consequence, the C-induced high-frequency band remains quite sharp and a big gap exists in the phonon density of states even up to a quite high concentration ($x \approx 0.8$) of C atoms. This very-low-phonon-density region should be detectable in the experimental measure-

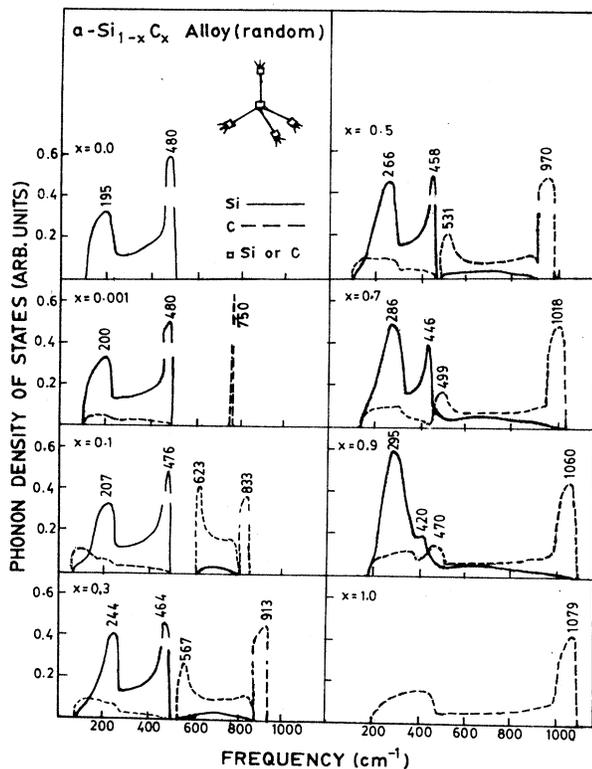


FIG. 1. Local phonon density of states (DOS) at Si (—) and C (---) atoms in α -Si_{1-x}C_x random alloys.

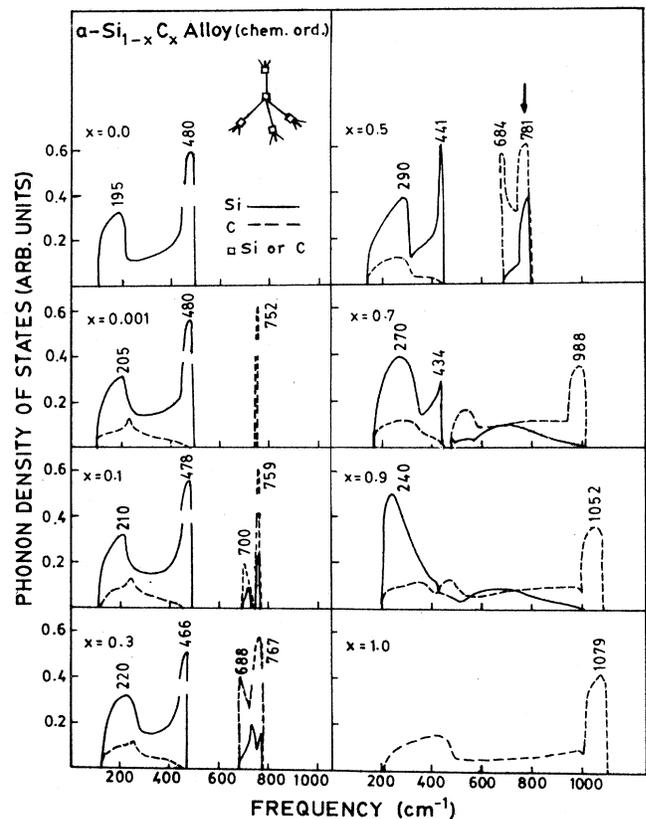


FIG. 2. Local phonon DOS at Si (—) and C (---) atoms in α -Si_{1-x}C_x chemically ordered alloys. Arrow indicates the experimental peak (Ref. 15).

ments in case the silicon-carbon alloys contain a chemically ordered configuration of the Si and C atoms.

C. $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys

For the calculation of the H-induced modes in $a\text{-SiC}$, we have used the observed peaks in the infrared data reported by Della Sala *et al.*⁹ as a guide. We assign 2100 cm^{-1} to the stretching vibration of the Si—H bond in the monohydride complex and enhance the Si—H stretching force constant (α) to reproduce the experimental value at 2100 cm^{-1} . The enhancement is understandable, as the C atom is more electronegative compared to the Si atom, which results in transfer of electronic charge from Si to C, making the Si—C bond ionic. The Si atom thus acquires more positive charge and is coupled to the negatively charged H atom more strongly. It leads to contraction in the Si—H bond length in comparison to that seen in the pure $a\text{-Si}$ network.

Further, the second-neighbor interaction $K_1(\text{C—Si—H})$ between the negatively charged C and H atoms will be larger compared to $K_1(\text{Si—Si—H})$ present in the pure $a\text{-Si}$ network, as the next-nearest-neighbor Si atom of the H atom is not positively charged. It also leads to an enhanced value for the angle-bending force constant, i.e., $K_1(\text{C—Si—H}) > K_1(\text{Si—Si—H})$. This effect has been observed by Della Sala *et al.*⁹ in their infrared transmission data of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys where, in Si-rich alloys, the Si-H wagging mode appears at $\sim 660\text{ cm}^{-1}$. We have thus increased the value of $K_1(\text{C—Si—H})$ over $K_1(\text{Si—Si—H})$ to reproduce the mode at the experimental value.

For dihydride (SiH_2) and trihydride (SiH_3), we have taken over the value of $K_3(\text{H—Si—H})$ from the hydrogenated $a\text{-Si}$ alloys because the presence of C atoms as the nearest neighbors of the Si atom will not have any effect on the H atoms, which in turn is expected not to alter the value of the force constant $K_3(\text{H—Si—H})$. The used values of the force constants are shown in Table I.

In the chemically ordered configuration of atoms where a minority atom is coupled always to the atoms in the majority as nearest neighbors, the results are slightly different. The interaction between the localized modes (appearing at $\sim 750\text{ cm}^{-1}$) originating from the isolated C atoms is weaker than that seen earlier in the random network. As a consequence, the C-induced high-frequency band remains quite sharp and a big gap exists in the phonon density of states even up to a quite high concentration ($x \approx 0.8$) of C atoms. This very low phonon density region should be detectable in the experimental measurements, in case the silicon-carbon alloy contains a chemically ordered configuration of the Si and C atoms.

1. Monohydrides (SiH and CH)

a. SiH complex. For a single H atom coupled to Si atom (SiH) in $a\text{-Si}_{1-x}\text{C}_x$ alloys (see Fig. 3) the bond-stretching and the bond-bending frequencies of the Si—H bond were reproduced at 2100 and 660 cm^{-1} , observed by Della Sala *et al.*⁹ for $x = 0.35$. The bond-stretching

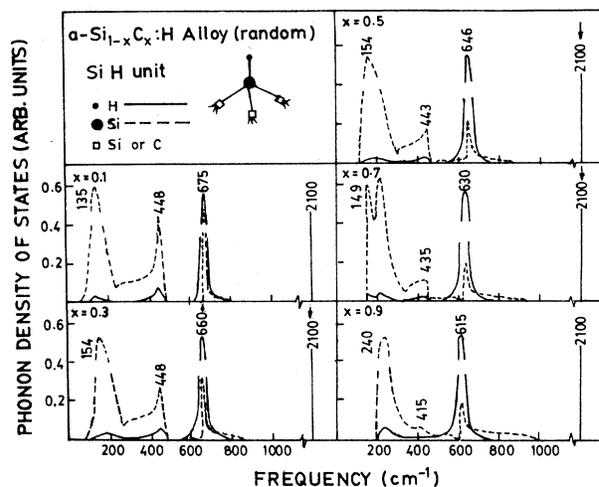


FIG. 3. Local phonon DOS at Si (---) and H (—) atoms for the SiH unit in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peaks (Ref. 9).

frequency remains unaffected by the presence of the C atoms lying in the nearest-neighbor sites of the reference Si atom. On the other hand, the wagging-mode frequency decreases from 675 to 615 cm^{-1} , with the increase in the concentration of C atoms. In fact, the wagging mode has not been detected in the experimental measurements for high values of x .

The H atom, being quite light in mass, is expected to affect the phonon density in a manner very much similar to that of a dangling bond. The states near the top of the phonon band are shifted to the low-frequency side, peaking around 135 cm^{-1} .

b. CH complex. For a H atom coupled to a C atom, i.e., for a CH unit (see Fig. 4), the behavior is very much similar to that of a SiH complex. The C—H bond-

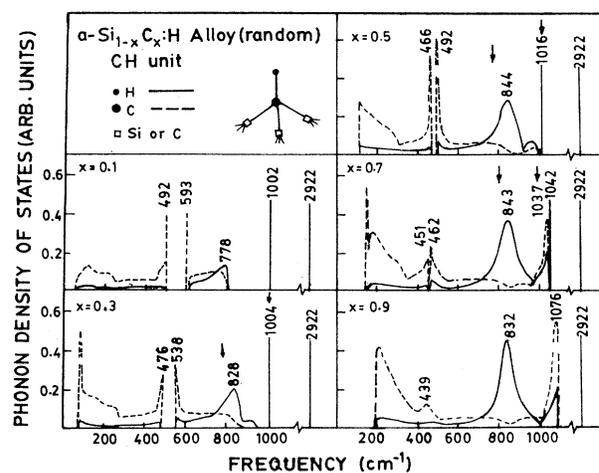


FIG. 4. Local phonon DOS at C (---) and H (—) atoms for the CH unit in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peaks (Ref. 9).

stretching frequency has been obtained at 2922 cm^{-1} by fitting the radial force constant. This value of the force constant reproduces well the two symmetric and asymmetric stretching frequencies at the measured frequencies for the CH_2 complex to be discussed later.

The C-H wagging mode is reproduced at 1002 cm^{-1} for $x=0.1$ by selecting an appropriate value of $K_1(\text{Si}-\text{C}-\text{H})$. Again, the C-H wagging-mode frequency varies with x in the entire concentration range. Similar to the SiH complex, enhancement in the local phonon density appears in the low-frequency region. A broad peak near $830\text{--}840\text{ cm}^{-1}$ in the bulk phonon region appears ($x > 0.2$) for the monohydride CH complex.

The results obtained for the monohydrides, SiH, and CH, both in the random and the chemically ordered atomic configurations of Si and C atoms, are quite similar, barring a notable difference for the CH complex in the bulk phonon region. A broad peak around the $830\text{--}840\text{ cm}^{-1}$ region is seen to appear for a low-C concentration ($0.2 < x < 0.5$) for the random sequence, but for the chemically ordered sequence, the same is observed only for a higher-C concentration ($x > 0.5$). The infrared data of Della Sala *et al.*⁹ reveals a broad peak around 770 cm^{-1} , even for a low-C concentration, $x=0.35$ [for comparison, one should note that x in the present paper is $(1-x)$ in Della Sala's paper]. This indicates the occurrence of a random distribution of Si and C atoms in the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys.

2. Dihydrides (SiH_2 and CH_2)

The values of force constants $\alpha(\text{Si}-\text{H})$ or $\alpha(\text{C}-\text{H})$ and of $K_1(\text{C}-\text{Si}-\text{H})$ or $K_1(\text{Si}-\text{C}-\text{H})$ fitted earlier for the monohydrides are then utilized to calculate the frequencies of the modes of the dihydrides. A value of $K_3(\text{H}-\text{Si}-\text{H})$ chosen earlier to reproduce the experimentally observed doublets at $(845,890)$ and $(862,907)\text{ cm}^{-1}$ in pure $a\text{-Si:H}$ alloys is used here.

The local phonon density at Si and H atoms for the SiH_2 unit in $a\text{-Si}_{1-x}\text{C}_x$ alloys for $0.1 \leq x \leq 0.9$ has been shown in Fig. 5. The H-induced high-frequency localized modes lying outside the bulk phonon band remain unaffected.

Two groups, Tawada *et al.*⁸ and Della Sala *et al.*⁹ have detected peaks in the infrared data corresponding to the stretching and wagging vibrations of the isolated dihydrides or interacting dihydrides in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys. The location of the experimental peaks around 2100 cm^{-1} is in good agreement with the calculated frequencies of the symmetric and asymmetric stretching modes at 2088 and 2112 cm^{-1} . Also, the calculated peak at $\sim 900\text{ cm}^{-1}$ originating from the H-Si-H angle bending motion is in excellent agreement with a peak at 900 cm^{-1} observed in the ir data of Si-rich ($x=0.35$) alloys of Della Sala. A H-induced peak near 660 cm^{-1} is also in agreement with the experimental data. The phonon density increases further in the low-frequency region, a behavior similar to a silicon atom containing two dangling bonds.

For CH_2 unit, the results have been presented in Fig. 6. The calculated peaks for the CH_2 unit at 2960 and 2887

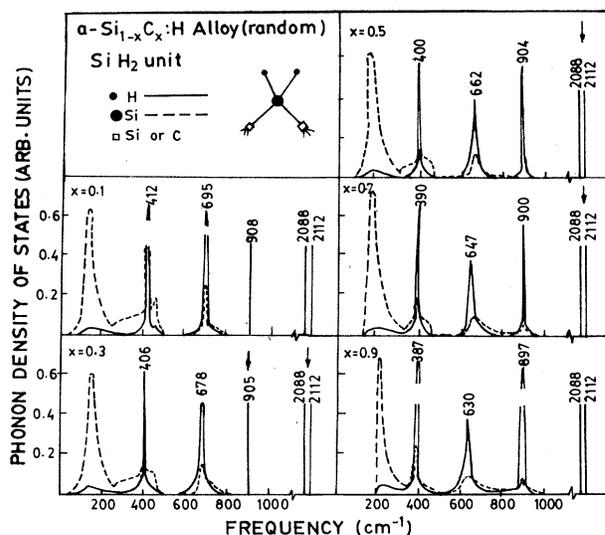


FIG. 5. Local phonon DOS at Si (---) and H (—) atoms for the SiH_2 unit in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peaks (Ref. 9).

cm^{-1} are in good agreement with the experimental values 2960 and 2900 cm^{-1} , respectively. The values of the angle-bending force constant $K_3(\text{H}-\text{C}-\text{H})$ is adjusted to reproduce the experimentally observed peak at 1401 cm^{-1} for the CH_3 unit, to be discussed later. The calculated peaks near 1070 and 1360 cm^{-1} are in good agreement with the observed peaks near 1000 and 1350 cm^{-1} .

3. Trihydrides (SiH_3 and CH_3)

The calculated local density of states at the Si and H atoms is shown in Fig. 7. For the SiH_3 unit, the calculated peaks corresponding to the asymmetric and symmetric

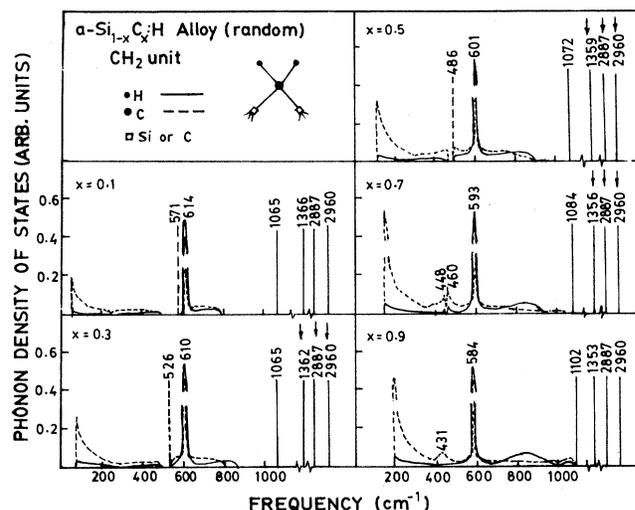


FIG. 6. Local phonon DOS at C (---) and H (—) atoms for the CH_2 unit in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peaks (Ref. 9).

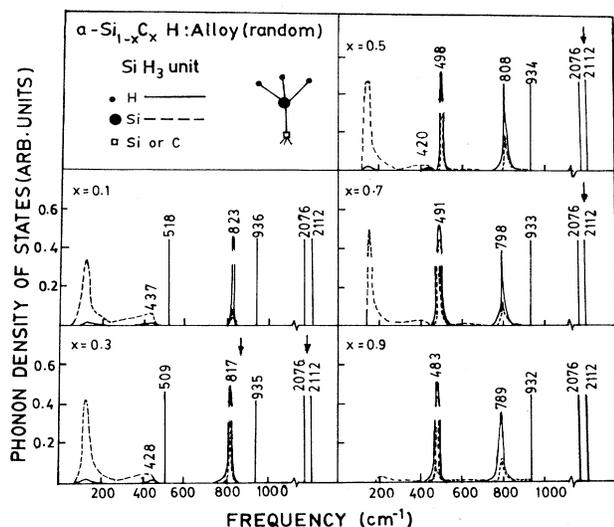


FIG. 7. Local phonon DOS at Si (---) and H (—) atoms for SiH_3 units in $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peak (Ref. 9).

stretching frequencies appear at 2112 and 2076 cm^{-1} , which are in agreement with the experimental data. Two other calculated peaks appear near 823 and 935 cm^{-1} , corresponding to the angle-bending motion of the trihydrides. In the infrared data, a peak does appear near 833 cm^{-1} .

For the CH_3 unit (Fig. 8), the calculated stretching-mode frequencies 2962 and 2848 cm^{-1} are in very good agreement with the experimental peaks near 2960 and 2898 cm^{-1} . The other two calculated peaks at 1400 and 1255 cm^{-1} originating from the angle-bending motions are in excellent agreement with their data⁹ peaks at 1400 and 1245 cm^{-1} .

III. CONCLUSIONS

In the present comprehensive study of the vibrational excitations of the hydrogenated amorphous $\text{Si}_{1-x}\text{C}_x$ alloys, we find that the H-induced localized vibrational

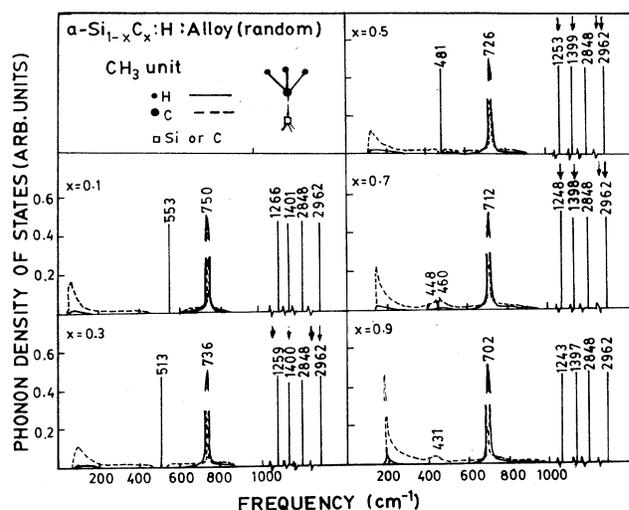


FIG. 8. Local phonon DOS at C (---) and H (—) atoms for the CH_3 unit in $\alpha\text{-Si}_{1-x}\text{C}_x\text{:H}$ random alloys. Arrows indicate the experimental peaks (Ref. 9).

modes lying outside the bulk phonon band region remain unaltered by the presence of the other kind of host atoms. However, a number of low-frequency inband modes incurred by H atoms change their locations with the relative concentrations of the constituent Si and C atoms. But these changes lie well within $\sim 10\%$. The calculated results are in good agreement with the available infrared data. However, a number of the predicted modes lying mainly in the bulk phonon band region have not been detected so far. More careful and detailed experimental investigations are very much needed to improve the present situation.

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¹Y. Kuwano, Tech. Dig. Int. PVSEC 1, 13 (1984).

²S. Tsuda *et al.*, Jpn. J. Appl. Phys. 21, Suppl. 21-2, 251 (1982).

³D. A. Anderson and W. E. Spear, Philos. Mag. 35, 1 (1977).

⁴H. Wieder, M. Cardona, and C. R. Guarnieri, Phys. Status Solidi B 92, 99 (1979).

⁵A. Guivaruch, J. Richard, M. LeContellec, E. Ligeon, and J. Fontenille, J. Appl. Phys. 51, 2167 (1980).

⁶Y. Catherine and G. Turban, Thin Solid Films 70, 101 (1980).

⁷Y. Katayama and T. Shimada, Jpn. J. Appl. Phys. 19, Suppl. 19-2, 115 (1980).

⁸V. Tawada, K. Tsung, K. Kondo, H. Okamoto, and Y. Hamakawa, J. Appl. Phys. 53, 5273 (1982).

⁹D. Della Sala, P. Fiorini, A. Frova, A. Gregori, A. Skumanich,

and N. M. Amer, J. Non-Cryst. Solids 77&78, 853 (1985).

¹⁰R. Dutta, P. K. Banerjee, and S. S. Mitra, Phys. Rev. B 27, 5032 (1983).

¹¹Bal K. Agrawal, P. S. Yadav, and B. K. Ghosh, J. Phys. C 21, 3397 (1988).

¹²Bal K. Agrawal, B. K. Ghosh, and P. S. Yadav, Phys. Rev. B 37, 10729 (1988).

¹³Bal K. Agrawal and Savitri Agrawal, Phys. Rev. B 36, 2799 (1987).

¹⁴B. K. Ghosh and Bal K. Agrawal, Phys. Status Solidi B 146, 148 (1988).

¹⁵Y. Katayama and T. Shimada, Jpn. J. Appl. Phys. 19, Suppl. 19-2, 115 (1980).