PHYSICAL REVIEW B VOLUME 22, NUMBER 6 15 SEPTEMBER 1980

Far-infrared absorption of pure and hydrogenated *a*-Ge and *a*-Si

S. C. Shen,* C. J. Fang,† M. Cardona, and L. Genzel
Max-Planck-Institute für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany
(Received 2 April 1980)

The far-infrared spectra of pure and hydrogenated *a*-Ge and *a*-Si have been measured with a double-beam, optically compensated Fourier-transform method. In addition to the standard TA-LA-LO-TO absorption bands, "critical-point" structures are observed for the TA bands and also their suppression upon hydrogenation. A local mode, attributed to clusters of four hydrogen atoms, appears at the top of the TA band. These results are discussed in the light of lattice-dynamical calculations for mass defect clusters.

I. INTRODUCTION

The disorder-induced one-phonon absorption of amorphous Ge and Si has been reported by several groups.[1-5] The lack of long-range order relaxes the crystal momentum and symmetry selection rules and results in dipole-allowed photon absorption with creation of a phonon. This process is forbidden in the corresponding crystalline materials. The only selection rule which applies to this absorption process in the amorphous materials is energy conservation.

It is well established that the tetrahedral short-range order is nearly preserved in amorphous Ge and Si. As a result, the density of vibrational states of these materials is a broadened version of that of their crystalline counterparts. The disorder-induced one-phonon absorption spectra of *a*-Ge and *a*-Si should represent that density of states modulated by transition matrix elements and statistical factors. These matrix elements are, however, relatively weak throughout the whole phonon spectrum as a result of the fact that they should vanish for perfect tetrahedra, i.e., in the crystalline counterparts (this is not the case in polar material such as GaAs).[4,6] Consequently the measurements, which have to be performed on thin films and in the far infrared, are difficult and considerable discrepancies exist among the various reported results.

In this paper, we present the disorder-induced one-phonon absorption spectra of pure and hydrogenated *a*-Ge and *a*-Si in the region from 15 to 550 cm^{-1}. The experiments were carried out with a double-beam, optically compensated Fourier-transform spectrometer which has been proved to be about five to ten times more sensitive in measuring weak absorptance than usual Fourier-transform spectrometers.[7,8] It is found that the disorder-induced one-phonon absorption and far-infrared spectra of *a*-Ge and *a*-Si are rather similar. In addition to the standard TA-LA-LO-TO absorption bands which have already been reported in ir absorption[1-5,8] and in Raman scattering experiments,[9,10] we observe in the nonhydrogenated materials substructure in the TA band which is suggestive of critical points in the crystal [such as TA (L) and TA (W)]. Upon hydrogenation the strength of the whole absorption spectrum decreases except for the appearance of a rather sharp peak centered at 116 cm^{-1} in Ge and 213 cm^{-1} in Si. These peaks, which have already been seen in the Raman spectra,[10] are attributed here to local modes of $(SiH)_4$ radicals which are pulled out of the TA band by the hydrogen.

The decrease of the absorption spectrum upon hydrogenation is largest for the "LA" band which is definitely shifted to lower frequencies when compared with the corresponding peak in the density of phonons of the crystalline materials. The "critical-point" structure of the TA band is suppressed by hydrogenation. These results are discussed in the light of lattice-dynamical calculations for *a*-Si clusters.[11,12] It is concluded by comparison with the work of Ref. 12 that the mechanism responsible for the disorder-induced lattice charge is mainly to be found in the distortions of the angles between bonds.

II. EXPERIMENT

The samples were prepared by rf sputtering, *a*-Ge onto high-purity crystalline Ge substrates and *a*-Si onto high-purity crystalline silicon. The substrate thickness was 0.2 mm. Sample *a*-Ge (1) was prepared in a pure-Ar atmosphere (0.01 Torr). Samples *a*-Ge (2), *a*-Ge (3), and *a*-Ge (4) were prepared by the same procedures in an Ar-H_2 mixture (0.01 Torr) with a partial pressure of H_2 of 2×10^{-4}, 1×10^{-3}, and 2.5×10^{-3} Torr, respectively. All *a*-Si samples were also prepared in Ar-H_2 mixtures with different partial pressures of H_2. The hydrogen contents in the samples were estimated from ir bond-wagging bands which occur between 500 and 700 cm^{-1}.[13,14] Some of the sputtering parameters and characteristics of the samples are listed in Tables I and II.

TABLE I. The sputtering parameters and some characteristics of the a-Ge films used. The substrates are 0.2 mm thick and were held at room temperature during sputtering.

Sample number	Ar pressure (Torr)	H_2 pressure (Torr)	Deposition rate (μm/hour)	Thickness (μm)	Concentration of hydrogen (at. %)
1	1×10^{-2}	0	2	30	0
2	1×10^{-2}	2×10^{-4}	2	15	6.1
3	1×10^{-2}	1×10^{-3}	2	15	7.4
4	1×10^{-2}	2.5×10^{-3}	0.6	3	10.3

The thicknesses of the samples were estimated with a stylus-type gauge (Tallysurf). Some of the samples show, in the near and middle infrared, interference oscillations from which the thicknesses can also be estimated. These two estimates are consistent within the experimental error of about 10–15%.

The absorption spectra of the amorphous films were measured with a double-beam, optically compensated Fourier-transform spectrometer which has been recently developed and described elsewhere.[7,8] A Perkin-Elmer Model 283 spectrometer was used in the wave-number region 350–550 cm^{-1}. With both instruments, the whole spectra from 15 to 550 cm^{-1} were obtained.

Interferences which come from multiple reflections within the substrates, and sometimes even within the films, are a serious problem for far-induced measurements. In this work the influence of interferences which come from multireflections within the substrates is mostly eliminated by the optical compensation of the instrument (a blank substrate of the same thickness as that for the sample is placed in the reference beam).[8] The interferences which come from the multireflection within the amorphous films depend upon the difference in refractive indices between the amorphous film and the substrate which may differ from sample to sample.[2,15] This difference is in any case very small, especially for a-Ge without H_2 or a-Ge and a-Si prepared with a low partial pressure of hydrogen; these samples did not show any effect of interferences within the amorphous film in the whole region of measurement. Some of the samples, for example, a-Si prepared in pure-Ar atmosphere show weak interference oscillations, whose magnitudes are much smaller than the main disorder-induced phonon-absorption bands, but are nevertheless comparable with some of their details (e.g., the critical-point structure of the TA bands). The effect of these interferences was corrected by extrapolating the interference oscillations observed in the middle infrared to the far infrared.

Owing to the high accuracy of the compensation method and the instrument used, the accuracy of the absorptance $(1-T)$ measurements of the amorphous films is better than 1% but the absolute accuracy of the absorption coefficient is much lower than this figure due to the experimental error of the thickness measurements of the film. The measurements for a-Ge in the wave-number region 260–300 cm^{-1}, where the crystalline Ge substrate has a rather low transmission due to two-phonon absorption, require such high accuracy.

III. RESULTS

The absorption spectra of a-Ge samples with different concentrations of hydrogen is shown in Fig. 1. For comparison we have also included in this figure the phonon density of states of crystalline Ge.[16] For pure amorphous Ge, there are three main absorption bands centered at 88, 170, and 280 cm^{-1} (see Table III) which are quite similar to those reported in the literature.[1-3,5] In

TABLE II. The sputtering parameters and some characteristics of the a-Si films used. The substrates are 0.2 mm thick and were held at room temperature during sputtering.

Sample number	Ar pressure (Torr)	H_2 pressure (Torr)	Deposition rate (μm/hour)	Thickness (μm)	Concentration of hydrogen (at. %)
1	2×10^{-2}	0	~2	15	0
2	2×10^{-2}	4×10^{-4}	2	15	19.6
3	2×10^{-2}	2×10^{-3}	2	15	24.2
4	1×10^{-2}	1×10^{-3}	0.8	6	15

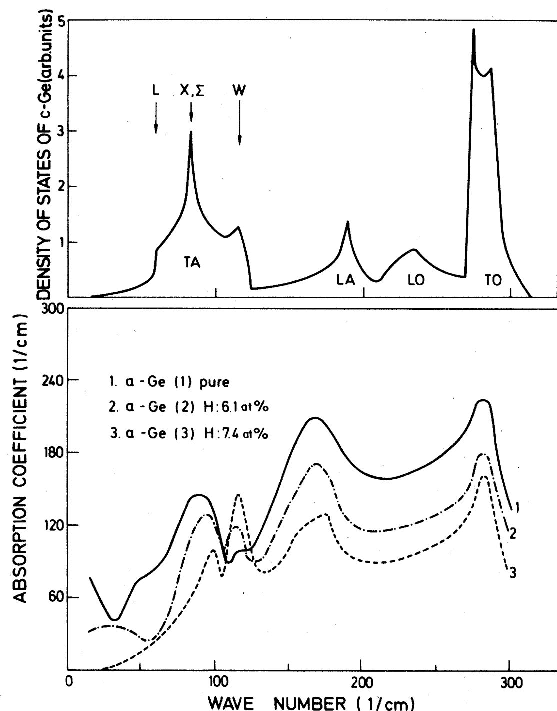

FIG. 1. The vibrational absorption spectra of pure and hydrogenated a-Ge. Included are the density of states of c-Ge (from Ref. 16) and the positions of some of its critical points.

addition, in the low wave-number region, there is an absorption shoulder centered at 50 cm^{-1}. A weak peak is also seen around 120 cm^{-1}. With hydrogenation, the shoulder at 50 cm^{-1} disappears, but the absorption feature around 120 cm^{-1} increases with increasing H concentration and develops into a well-defined absorption peak at 116 cm^{-1}. Except for this peak, the rest of the spectrum decreases upon hydrogenation. This decrease is particularly striking for the band at ~170 cm^{-1}, which is labeled as LA in Table III by analogy with the density of phonons of crystalline Ge.

Figure 2 shows the spectra of a-Si samples with several concentrations of hydrogen. Again, the phonon density of states of crystalline Si is shown for comparison. The absorption features of a-Si are quite similar to those of a-Ge (see also Table III). An absorption shoulder or plateau is observed in the low-frequency side of the TA band, now centered at 130 cm^{-1}. This shoulder or plateau also weakens and even disappears with increasing hydrogenation. On the high-frequency side of the TA band there is also a weak shoulder centered at 210 cm^{-1}. Upon hydrogenation, a strong peak develops out of this feature. For a hydrogen concentration of 20% in the sample, the strength of this peak is almost double that of the original TA band of pure a-Si. As in the case of a-Ge, the rest of the spectrum, and especially the LA band, decreases with increasing concentration of hydrogen. Some absorption features have also been observed in the very far infrared (below 50 cm^{-1} for a-Ge and below 100 cm^{-1} for a-Si), which are certainly not attributed to vibrational modes but associated with electronic processes and will be discussed elsewhere.

IV. DISCUSSION

We have listed in Table III the positions of the features observed in Figs. 1 and 2 for the pure and the most hydrogenated a-Ge and a-Si samples. For the sake of comparison we have added to this table the wave numbers of the corresponding peaks observed in the Raman spectra of pure and highly hydrogenated a-Ge and a-Si.[10] We have also listed the wave numbers of the peaks observed in the density of states of c-Ge and c-Si. Because of the close correspondence between peaks in the ir and Raman spectra of pure a-Ge and a-Si and the density of phonon states of the crystalline materials, we label the peaks of the amorphous materials following the crystalline notation (TA-LA-LO-TO).

We have listed in the last two lines of Table III the ratio of the wave numbers of the ir peaks of a-Si to those of a-Ge and the corresponding ratio for the peaks in the densities of states of crystalline materials. With the exception of the TA (L) shoulder for the amorphous spectra, the correspondence is very good. The average value of the amorphous ratio is 1.79, that of the crystalline 1.78. This number should equal[10]

$$\left(\frac{m_{Ge}}{m_{Si}}\right)^{1/2}\left(\frac{a_0(\mathrm{Ge})}{a_0(\mathrm{Si})}\right)^{1.5}=1.71\,, \qquad (1)$$

where m represents the atomic mass and a_0 the lattice constant. The result of Eq. (1) agrees well with the value given above within the dispersion of the data of Table III.

A rather interesting fact is that the ratio of wave number of the "local" modes (L), 1.83 according to Table III, is also very close to the estimate of Eq. (1). This suggests that this mode, while induced by the presence of hydrogen, does not correspond to a vibration mainly of the hydrogen but to a vibration in which the mass of the host atoms plays a decisive role, i.e., an extended local mode around the hydrogen atoms. The position of this peak at the top of the TA bands in a region where the density of states falls to *nearly* zero qualifies it as a near-gap state.

It has been recently shown (Ref. 14, Fig. 9) that at moderately high H concentrations, four

TABLE III. The positions of the features observed in ir and Raman spectra for the pure and hydrogenated a-Ge and a-Si. [a]

Absorption feature Sample	TA (L)	TA (X)	TA (W)	Local	LA	LO	TO
	Positions of absorption features (cm^{-1})						
ir pure a-Ge (1)	50	88	120		170	240	280
Raman pure a-Ge		80			177	230	278
Density of states c-Ge	61	80	111		189	235	282
ir hydrogenated a-Ge (3)		98		117	175	240	278
Raman hydrogenated a-Ge		82		115	177		278
ir pure a-Si (1)	130	180	210		300	392	465
Raman pure a-Si		150			310	380	480
Density of states c-Si	110	160	215		325	390	480
Density of states a-Si	120	185			310	400	490
ir hydrogenated a-Si (3)				211	310		460
Raman hydrogenated a-Si		150		215	310	410	480
Ratio $\omega(Si)/\omega(Ge)$ (ir)	2.60	2.05	1.79	1.83	1.77	1.63	1.65
Ratio $\omega(Si)/\omega(Ge)$ (Density of states, crystalline)	1.80	2.00	1.90		1.72	1.66	1.70

[a] The ir results are from this work; the Raman results are those of Ref. 10. The peaks in the densities of crystalline states are from Ref. 16. The peaks in the density of states of a-Si are from Ref. 12.

hydrogen atoms tend to cluster as they saturate groups of four dangling bonds pointing towards a Si (or Ge) vacancy. We now explore the possibility of the L mode being associated with these $(SiH)_4$ clusters. Such association would explain, at least qualitatively, the delay in the appearance of L found with increasing H concentration; L appears first for $H \sim 5.0\%$ (see Fig. 3), i.e., for an average H separation of 7.3 Å. The diameter of the Si_4 + vacancy cluster is ≃six times the covalent radius of Si = 7.04 Å. Hence it is reasonable to assume that the four dangling bonds in the cluster will be automatically saturated by H if the average distance between H atoms is approximately equal to the diameter of the cluster. At smaller H concentrations the four dangling bonds associated with a vacancy will not all be saturated. In fact, one will find a large number of them with only one hydrogen. We believe this may be the cause of the strong increase in the apparent oscillator strength of the SiH bond-stretching band (2000 cm^{-1}) found in Ref. 14 (see Fig. 3 of this reference) for less than 10% H.

We now proceed to calculate the frequency of the local mode associated with the $(SiH)_4$ clusters. Because of the low frequencies involved, we treat the four H atoms as a *single particle* of mass four. The topology becomes again that of perfect-tetrahedral unhydrogenated silicon. An examination of the high-frequency local modes of Si-H discussed in Ref. 17 shows that the bond-stretching and bond-bending force constants are close to those for Si-Si (or Ge-Ge) bonds.[17] We can thus treat the H_4 cluster as a mass defect of

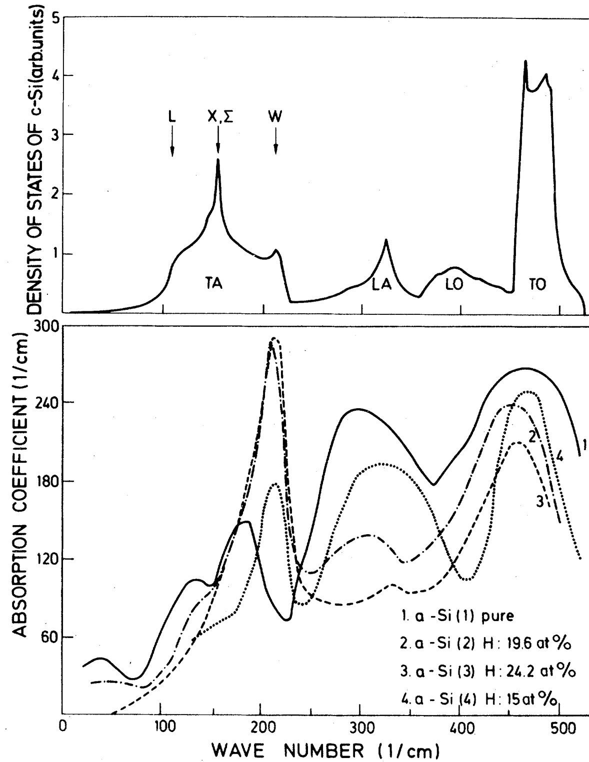

FIG. 2. The vibrational absorption spectra of pure and hydrogenated a-Si. Included are the density of states of c-Si (from Ref. 16) and the positions of some of its critical points.

mass 4. The local mode frequency is then obtained from the secular equation[18,19]:

$$\frac{\epsilon\omega^2}{6}\int\frac{g(\omega')d\omega'}{\omega^2-\omega'^2}=1\ , \tag{2}$$

where ϵ, the mass defect, is given by

$$\epsilon=(M-M_H)/M\ , \tag{3}$$

with M_H the mass of the hydrogen cluster and $g(\omega)$ the density of phonon states per primitive cell.

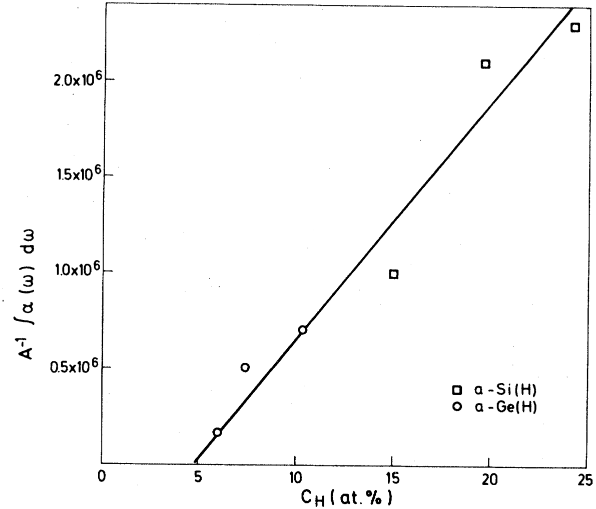

FIG. 3. The variation of the quantity $A^{-1}\int\alpha\,d\omega$ of the local mode with the concentration of hydrogen. A is the parameter which determines the amplitude of the local mode [Eq. (6)], α the absorption coefficient.

When integrating the nearly vertical upper flank of the TA bands of Figs. 1 and 2 we obtain a logarithmic singularity, and consequently Eq. (2) *always* has a solution (local mode) for the case of a mass defect very near the upper flank of the TA density of states (W points of Table III). These considerations suffice to explain qualitatively the L modes under discussion. For the purpose of evaluating analytically the integral of Eq. (2) we replace the TA density of states by a rectangle with the upper flank ω_M at the W point and the lower flank at $\omega_m=100\ \mathrm{cm}^{-1}$ for Si and $60\ \mathrm{cm}^{-1}$ for Ge. The height H of the rectangle is obtained from the normalization

$$\int_{\omega_m}^{\omega_M} g(\omega')d\omega'=2=H(\omega_M-\omega_m)\ , \tag{4}$$

TABLE IV. Summary of ir absorption intensities $I=\int\alpha\,d\omega$ (in cm^{-2}) of the bond-bending bands I_B, wagging bands I_w, and the local mode I_L. Here A is the parameter which determines the amplitude of the local mode (Eq. 6).

Sample	I_B	I_w	I_L	$A^{-1}I_L$	$A^{-1}I_L/I_w$	C_H (%)
a-Ge (1)						
a-Ge (2)	2.5×10^2	1.4×10^5	2.5×10^2	1.7×10^5	1.2	6.0
a-Ge (3)	8.2×10^2	1.8×10^5	7.7×10^2	5.1×10^5	2.8	7.4
a-Ge (4)	2.5×10^3	2.4×10^5	1.05×10^3	7.0×10^5	2.9	10.3
a-Si (1)						
a-Si (2)	1.4×10^4	3.9×10^5	8.6×10^3	2.1×10^6	5.3	19.6
a-Si (3)	2.8×10^4	4.8×10^5	9.3×10^3	2.3×10^6	4.8	24.2
a-Si (4)	1.4×10^4	3.0×10^5	3.9×10^3	1.0×10^6	3.3	15.0

i.e.,

$$H = 2/(\omega_M - \omega_m).$$

The secular equation (2) thus becomes

$$\frac{\epsilon\omega}{6(\omega_M - \omega_m)} \ln \frac{(\omega + \omega_M)(\omega - \omega_m)}{(\omega - \omega_M)(\omega + \omega_m)} = 1. \quad (5)$$

Equation (5) can be solved numerically. For $\omega_M = \omega_{TA}(W)$ of Table III we find $\omega_L = 224$ for Si and $\omega_L = 124$ for Ge, in excellent agreement with the experiments.

The amplitude of the L-mode vibrations can also be evaluated with the methods of Refs. 18 and 19. We find for each of the three degenerate vibrations of the H_4 cluster the zero-point amplitude

$$|u|^2 \simeq A(\hbar/2\omega_L M) \quad (6)$$

with $A = 1.5\times10^{-3}$ for Ge and $A = 4\times10^{-3}$ for Si. The vibrational amplitude on the neighboring Si (Ge) atoms decays exponentially upon moving away from the H. The decay length is $\simeq 7$ Å (for Si) and hence the local vibrations extend to the fourth neighbors of the H cluster (a total of 60 atoms involved).

We show in Table IV the integrated strength $I = \int \alpha\, d\omega$ (in cm^{-2}) of the L modes as observed and also this strength divided by A. The latter quantity is proportional to the square of the effective charge[17] which is expected to be nearly the same for a-Ge as for a-Si. We also list in this table the corresponding numbers for the wagging and the bending ($=SiH_2$) bands and the hydrogen concentration. The bending bands are much weaker than the L bands (after normalization by A), hence we can dismiss these bands (i.e., $=SiH_2$ groups) as the source of the local modes under consideration; the latter could not become ir active by borrowing oscillator strength from the much weaker $=SiH_2$ groups. Hence we conclude that the L modes are associated with $(Si)_3$-Si-H types of groups. According to Table IV the wagging modes have enough ir strength to lend a fraction of it to the L modes.

We display in Fig. 3 the quantity $A^{-1}\int \alpha\, d\omega$ as a function of hydrogen concentration determined from the strength of the wagging bands for our Ge and Si samples.[3] A straight line can be drawn through all points, those for Ge and those for Si, as expected. This would not be the case if we had plotted $A^{-1}\int \alpha\, d\omega$ as a function of the concentration of GeH_2 (or SiH_2) groups ($\propto$ to the strength of the bond-bending bands). Figure 3, however, indicates that a minimum H concentration is needed for the "local mode" to appear.

We would now like to interpret qualitatively the strength of the ω_L bands. We suppose that their ir activity arises from the dynamical charge for the bond-wagging modes as ω_L must involve almost exclusively angular motions without stretch. In this case the ratio R:

$$R = I_L / A I_w \quad (7)$$

should be of the order of 1. The values of the ratio in Eq. (7) are shown in Table IV. They are indeed of the order of unity, as expected.

We note that the ESR signal of a-Ge disappears for a hydrogen concentration of ~5%,[20] in agreement with our assignment of the ω_L vibration; at this concentration (see Fig. 3) all four dangling bonds associated with vacancies are saturated by hydrogen.

We discuss finally the ir features other than ω_L in Figs. 1 and 2. The ir spectrum of a-Si has been calculated for 61- and 62-atom clusters in Ref. 12. Although these spectra exhibit the TO and LA features, the TA band is completely absent, while in Fig. 1 it appears quite prominently. We believe this discrepancy is an artifact of the calculation which makes an "ansatz" for the dipole moment dependent only on disorder-induced fluctuations in the *bond lengths*. It is well known, however, that the bond lengths of Ge and Si are rather rigid and that the disorder is produced mainly by fluctuations in the bond and dihedral angles. These fluctuations can even be macroscopic, such as those involved in changes between chair-boat and staggered-eclipsed configurations. The ansatz in Ref. 12 is such that only *bond-stretching* vibrations produce a dipole moment [Eq. (5) of Ref. 12 contains only scalar products of bond lengths and phonon displacements]. It is thus quite clear that this is not the mechanism responsible for the observed dipole absorption. A further discussion of this point must await a calculation including charges induced by angular fluctuations.

One of the most interesting features of Figs. 1 and 2 is the decrease in the strength of TA, LA, LO, and TO bands upon hydrogenation, especially the two former ones. It is easy to speculate about one of the sources of this decrease; hydrogenated samples have less internal tensions and some of the angular distortions responsible for the dipole moment can relax. This fact, however, would probably result in a uniform decrease throughout the whole spectrum (except for ω_L). Such angular relaxation is probably responsible for the decrease of the TO bands and this decrease can be used to estimate the amount of such relaxation [20% for sample Si (3)]. The additional decrease in oscillator strength of the TA and LA bands should be sought elsewhere.

We suggest as an explanation a decrease in the corresponding phonon density of states produced by the hydrogenation. Such decrease or blunting of the TA and LA bands has been pointed out by Yndurain and Sen[11] for the TA bands as a result of disturbing tetrahedra and for the LA bands as a result of breaking or opening bond rings.

ACKNOWLEDGMENTS

We would like to thank H. Bilz, J. Kuhl, and L. Ley for helpful discussions; T. P. Martin for a critical reading of the manuscript, and D. Böhme for technical assistance in the experiments.

---

*On leave from Shanghai Institute of Applied Physics, Academia Sinica, China.
†On leave from Chinese University of Science and Technology, Beijing, China.

[1]M. H. Brodsky and A. Lurio, Phys. Rev. B 9, 1646 (1974).
[2]P. C. Taylor and U. Strom, Phys. Rev. B 13, 1711 (1976).
[3]R. G. Buckley and H. J. Trodahl, Solid State Commun. 27, 283 (1978).
[4]W. Prettl, N. J. Shevchik, and M. Cardona, Phys. Status Solidi B 59, 241 (1973).
[5]R. W. Stimets, J. Waldman, J. Lin, T. S. Chang, R. J. Temkin, and G. A. N. Connell, Solid State Commun. 13, 1485 (1973).
[6]S. S. Mitra, D. K. Paul, Y. F. Tsay, and B. Bendow, in *Tetrahedrally Bonded Amorphous Semiconductors (Yorktown Heights)*, Proceedings of the International Conference on Tetrahedrally Bonded Amorphous Semiconductors, edited by M. H. Brodsky, S. Kirkpatrick, and D. Wearie (AIP, New York, 1974), p. 284.
[7]L. Genzel and J. Kuhl, Infrared Phys. 18, 113 (1978).
[8]S. C. Shen, T. Welker, J. Kuhl, and L. Genzel, Infrared Phys. (in press).
[9]J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder, M. I. Nathan, and A. Pinczuk, Phys. Rev. Lett. 26, 642 (1971).
[10]D. Bermejo and M. Cardona, J. Non-Cryst. Solids 32, 405 (1979).
[11]F. Yndurain and P. N. Sen, Phys. Rev. B 14, 531 (1976).
[12]R. Alben, D. Weaire, J. E. Smith, Jr., and M. H. Brodsky, Phys. Rev. B 15, 2271 (1975); D. Beeman and R. Alben, Adv. Phys. 26, 339 (1977).
[13]C. J. Fang, K. J. Gruntz, L. Ley, M. Cardona, F. J. Demond, G. Müller, and S. Kalbitzer, J. Non-Cryst. Solids 35, 255 (1980).
[14]H. R. Shanks, C. J. Fang, L. Ley, M. Cardona, F. J. Demond, and S. Kalbitzer, Phys. Status Solidi (in press).
[15]E. C. Freeman and W. Paul, Phys. Rev. B 20, 716 (1979).
[16]W. Weber, Phys. Rev. B 15, 4789 (1977).
[17]M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B 16, 3556 (1977).
[18]P. G. Dawber and R. J. Elliott, Proc. R. Soc. London A273, 222 (1963).
[19]F. Cerdeira, T. A. Fjeldly, and M. Cardona, Phys. Rev. B 9, 4344 (1974).
[20]J. Stuke, in *Amorphous and Liquid Semiconductors*, edited by W. E. Spear (University of Edinburgh, Edinburgh, 1977), p. 406.