

and nonresonant diffusion, is then calculated. It should be noted that the wave spectrum employed in our analysis contains a wide range in  $k$  space and there exist waves with small phase velocity, e.g.,  $v_{ph} = \omega_k/k \approx 0.6C_s$  for  $k = k_{20}$ , which can directly interact with ions. We find that the nonresonant diffusion is essential for the ion-tail formation. It is the nonresonant quasilinear diffusion that brings a small portion of ions into the ion-acoustic velocity range. Once an ion tail is formed by the nonresonant diffusion, the resonant interaction pulls more ions from the bulk into the tail.

In conclusion, we have found that quasilinear diffusion in velocity space is sufficient to explain the mechanism of high-energy ion-tail formation in current-driven ion-acoustic instability. The nonresonant quasilinear diffusion plays an important role in the early stage, and later both nonresonant diffusion mechanisms become important.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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<sup>6</sup>The electron distribution function revealed in computer simulations (see, for example, Ref. 5) is not pure Maxwellian and flattening at lower velocities takes place. This effect slightly reduces the growth rate of the instability and consequent complete stabilization which was not observed in the present study. As long as the mechanism of high-energy ion-tail formation is concerned, the small change in the growth rate does not appreciably affect the ion dynamics, and the Maxwellian assumption does not cause significant errors. Non-Maxwellian electron distribution, however, does govern the period of wave growth and final saturation. We are currently working on this problem by removing the Maxwellian constraint, and assuming a two-dimensional plasma. Results will be reported in a separate paper.

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## Vibrational Excitations in $a$ -Si:F and $a$ -Si:(F,H) Alloys

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(Received 4 September 1980)

The vibrational excitations, both in the Si-bulk band mode region and above it at the impurity centers in the various configurations for the  $a$ -Si:F and  $a$ -Si:(F,H) alloys, have been obtained by using a cluster Bethe-lattice method. The predicted frequencies are in excellent agreement with the available experimental data.

PACS numbers: 63.50.+x, 72.80.Ng

Amorphous silicon ( $a$ -Si) is well known to be a very promising material for low-cost solar cells and field-effect transistors (FET's) for display panels. Hydrogenated  $a$ -Si can be substitutionally doped, in contrast to  $a$ -Si, but the doping efficiency is much smaller because of, in part, the presence of the appreciable density of localized

states in the energy gap of  $a$ -Si; however, this density is reduced by the incorporation of hydrogen, but not completely removed. Madan and co-workers<sup>2</sup> have reported that the addition of fluorine to  $a$ -Si:H increases the doping efficiency of the material, and also that the  $a$ -Si:(F,H) alloys have much better thermal and mechanical stabil-

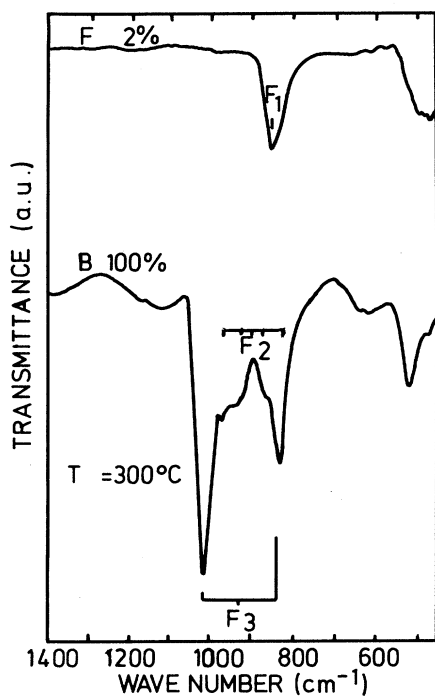


FIG. 1. Infrared transmission spectra of  $a$ -Si:F alloys measured by Shimada, Katayama, and Horigome (Ref. 5) for some  $\text{SiF}_4$ -Ar gas mixtures. The percentage shown in the figure is of  $\text{SiF}_4$  gas and the symbols  $F_1$ ,  $F_2$ , and  $F_3$  denote their assignment of the modes.

ities and less photo-structural changes than the  $a$ -Si:H alloys.<sup>2,3</sup> The alloys are highly photoconductive.

In order to understand the bonding configurations of F and H atoms in  $a$ -Si, some infrared absorption measurements in  $a$ -Si:F<sup>4,5</sup> and in  $a$ -Si:(F,H) alloys<sup>2,6,7</sup> have recently been made. Assignments of the observed lines to the various atomic configurations have also been made in these studies, although in some cases they are conflicting. From a theoretical point of view, in contrast to detailed cluster calculations for  $a$ -Si:H alloys,<sup>8,9</sup> very few calculations<sup>10,11</sup> have been reported for the Si:F system, and there is no detailed calculation of the vibrational excitations in  $a$ -Si:F and  $a$ -Si:(F,H) alloys. In the present paper, I present the results of such a study for these materials, using a cluster Bethe-lattice method. The method has been used successfully earlier for understanding the electronic and phonon properties of various inhomogeneous systems.

For the details of the cluster Bethe-lattice method I refer to earlier papers.<sup>12</sup> I reproduce

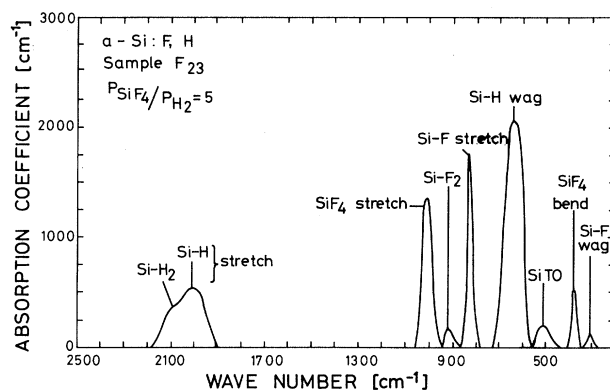


FIG. 2. Infrared absorption spectra of Fang *et al.* (Ref. 7) for  $a$ -Si:(F,H) alloys, along with their assignment. The present assignment is different for some modes (see Table I).

here a part of the measured infrared spectra of Shimada, Katayama, and Horigome<sup>5</sup> for  $a$ -Si:F alloys (Fig. 1), and of Ley *et al.*<sup>7</sup> for  $a$ -Si:(H,F) alloys (Fig. 2).

In earlier studies with my collaborators,<sup>13</sup> a four-parameter second-neighbor force model was seen to be quite successful in generating the phonon dispersion curves of Si and Ge in the symmetry directions. As the second-neighbor force constants are quite small, I consider here only the nearest-neighbor central and noncentral force constants. The phonon density of the Bethe-lattice model of bulk  $a$ -Si resembles closely the infrared data and TA and TO peaks appear at 200 and 510  $\text{cm}^{-1}$ , respectively. Calculations have been performed for the various configurations of Si, F, and H atoms, as shown in Figs. 3-5. The silicon atoms are connected to a Bethe lattice appropriate for bulk  $a$ -Si. The force constants chosen to reproduce the experimental frequencies are shown in Table I.

Figures 3 and 4 exhibit the phonon density of states at one Si atom and at one F atom in the  $\text{SiF}$ ,  $\text{SiF}_2$ , and  $\text{SiF}_3$  configurations. For  $\text{SiF}$ , I have reproduced a resonance near 300  $\text{cm}^{-1}$  and a localized mode at 830  $\text{cm}^{-1}$  (Table I). An impurity-activated TO peak of Si appears near 510  $\text{cm}^{-1}$  in the bulk-mode region. For the  $\text{SiF}_2$  configuration [Fig. 4(a)] one observes the resonance modes at 300 and 330  $\text{cm}^{-1}$ . The localized modes appear at 868 and 968  $\text{cm}^{-1}$ . For the  $\text{SiF}_3$  configuration [Fig. 4(b)], resonances appear at 300, 375, and 520  $\text{cm}^{-1}$ , and the localized modes at 839 and 1016  $\text{cm}^{-1}$ .

All the calculated localized-mode frequencies

TABLE I. Assignment of the measured frequencies against the various configurations in  $\alpha$ -Si:F and  $\alpha$ -Si:(F,H) alloys.  $\alpha$  and  $\beta$  denote the central and angular force constants, respectively.

Confi- guration	Force constants		Resonance and localized frequencies ( $\text{cm}^{-1}$ )	
	Bond	( $10^5$ dyn/cm)	Calculated	Measured
a-Si	Si-Si	1.40 0.17	510	490
SiF	Si-F	4.43 1.01	300	300 <sup>b</sup>
			830	850 <sup>a</sup> , 828 <sup>b</sup> , 830 <sup>c,d</sup>
SiF <sub>2</sub>	Si-F	5.40 1.01	300	300 <sup>b</sup>
			330	325 <sup>a</sup> (tentative)
			868	870 (827) <sup>a</sup>
			968	965, (920) <sup>a</sup> , 930 <sup>b</sup> , 950 <sup>c</sup> , 975 <sup>d</sup>
SiF <sub>3</sub>	Si-F	5.71 1.01	300	300 <sup>b</sup>
			375	380 <sup>b</sup>
			520	515 <sup>a</sup> , 510 <sup>b</sup>
			840	838 <sup>a</sup>
			1016	1015 <sup>a,d</sup> , 1010 <sup>b,c</sup>
SiFH	Si-H	2.27 0.43	529	515 <sup>a</sup> , 510 <sup>b</sup>
	Si-F	4.43 1.01	792	828 <sup>b</sup>
			877	890 <sup>b</sup> , 900 <sup>d</sup>
			902	
			2000	1985 <sup>b</sup> , 2000 <sup>d</sup>
SiF <sub>2</sub> H	Si-H	2.48 0.43	300	300 <sup>b</sup>
	Si-F	5.40 1.01	330	325 <sup>a</sup> (tentative)
			385	380 <sup>b</sup>
			529	515 <sup>a</sup> , 510 <sup>b</sup>
			820	828 <sup>b</sup>
			839	840 <sup>b</sup>
			908	890 <sup>b</sup> , 900 <sup>d</sup>
			992	975 <sup>d</sup>
			2090	2090 <sup>b</sup> , 2100 <sup>d</sup>

<sup>a</sup>Ref. 5.

<sup>b</sup>Ref. 7.

<sup>c</sup>Ref. 4.

<sup>d</sup>Ref. 6.

are in excellent agreement with the data of Shimada, Katayama, and Horigome<sup>5</sup> as is clear from Table I. The measured Si-F stretching frequency in the SiF configuration varies from 830 to 850  $\text{cm}^{-1}$  in the reported experimental data. It should be noted that a central force constant chosen for each configuration gives two localized frequencies in the SiF<sub>2</sub> and SiF<sub>3</sub> configurations, in agreement with the measured frequencies. These frequencies are not affected by the angular force constant which determines the resonance modes in the bulk-mode region. The twist mode at 330  $\text{cm}^{-1}$  is only Raman active and might be quite

weak in Raman spectra because of the matrix-element effect.

I then calculated the phonon density for the SiFH and SiF<sub>2</sub>H configurations [Figs. 5(a) and 5(b), respectively]. The central and angular force constants for the Si-H bond were first fitted to reproduce the experimental frequencies in SiH, SiH<sub>2</sub>, and SiH<sub>3</sub> configurations in pure hydrogenated Si material, i.e., 630 and 2000  $\text{cm}^{-1}$  for SiH, and 850, 890, and 2090  $\text{cm}^{-1}$  for SiH<sub>2</sub>. For the SiH<sub>3</sub> configuration, the calculated frequencies are 875, 910, and 2140  $\text{cm}^{-1}$ . For the SiH<sub>2</sub> and SiH<sub>3</sub> configurations, we also observe splittings

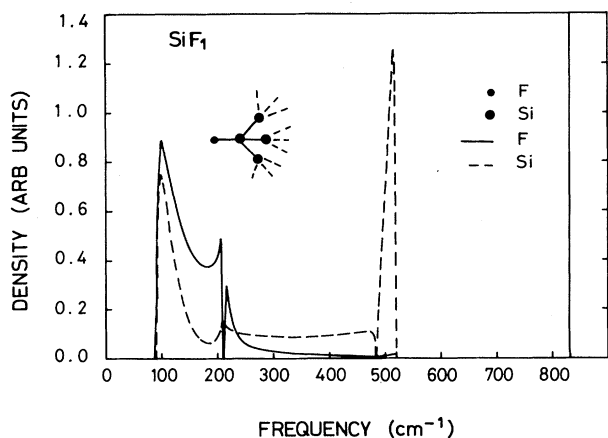


FIG. 3. Local phonon density of states for  $\text{SiF}_1$  configurations. The continuous and dashed curves depict the densities at F and Si atoms, respectively, for  $\alpha = 4.43 \times 10^5$  dyn/cm and  $\beta = 0.34 \times 10^5$  dyn/cm, where the resonance mode appears at  $224 \text{ cm}^{-1}$ . (The value of  $\beta$  is different here from that of Table I in the text.) The small dashed lines at Si atoms show the connection to the Bethe lattice.

of about  $20 \text{ cm}^{-1}$  in the bond-stretching vibrations and of about  $10\text{--}15 \text{ cm}^{-1}$  in some of the bond-bending vibrations. For the Si-F bonds, the values of the force constants were chosen similar to

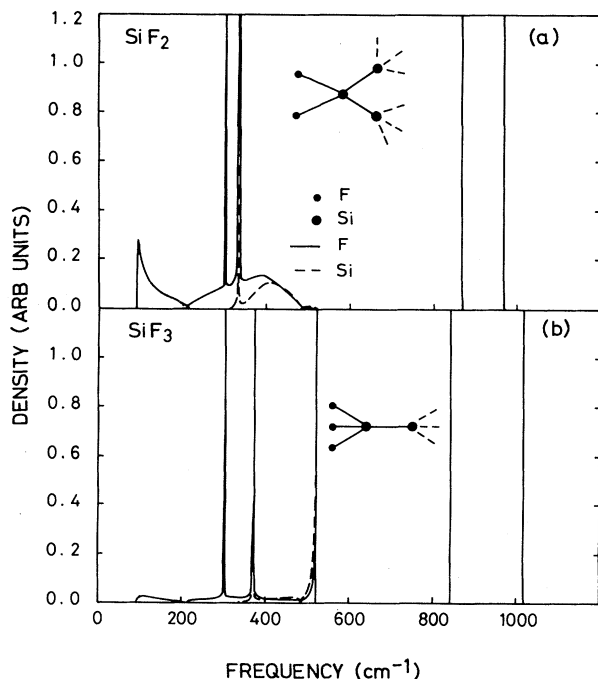


FIG. 4. Same for Fig. 3 except that this is for (a)  $\text{SiF}_2$  and (b)  $\text{SiF}_3$  configurations.

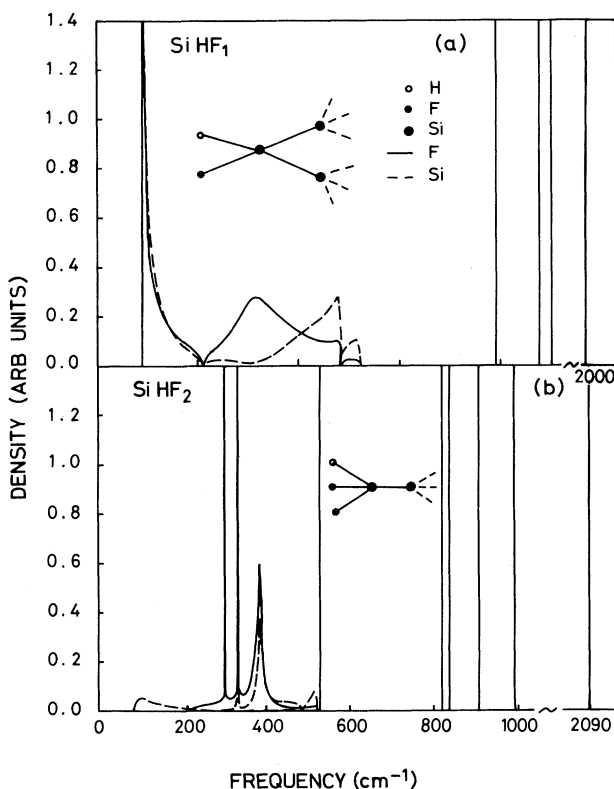


FIG. 5. Same for Fig. 3 except that this is for (a)  $\text{SiFH}$  and (b)  $\text{SiF}_2\text{H}$  configurations. The density at H atom appears mainly above the band-mode region.

the pure fluorinated Si materials.

The various resonance and localized modes for the  $\text{SiFH}$  and  $\text{SiF}_2\text{H}$  configurations are enumerated in Table I, along with the measured frequencies by different workers. The resonance frequencies at  $300$ ,  $380$ , and  $520 \text{ cm}^{-1}$  have been detected by Ley *et al.*<sup>7</sup> A perusal of Table I reveals that almost all the predicted frequencies have been seen in the infrared data.

In the above calculation for  $\text{Si}:(\text{F},\text{H})$  alloys, the interaction parameters used were those of the pure  $\text{Si}:\text{H}$  and  $\text{Si}:\text{F}$  systems. However, they might be affected by the induction effects<sup>11</sup> and other effects arising from the local environment, etc. The calculated frequencies will show some variation and may lead to the disappearance of some observed small discrepancies. It may be noted that the possible occurrence of unwanted impurities such as H and O in the measured samples (Figs. 1 and 2) may also give rise to peaks observed at  $650$  and  $1015 \text{ cm}^{-1}$ , and one should be quite careful while attempting an assignment.

The author is grateful to Professor J. L. Beeby,

University of Leicester, United Kingdom, for his hospitality. This work was supported in part by the Science Research Council, United Kingdom, and by the University Grants Commission, New Delhi, India.

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## Microscopic Model of Anomalous Low-Frequency Excitations in Inorganic Glasses: Molecular Dynamics Study of BeF<sub>2</sub>

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(Received 8 December 1980)

In molecular-dynamics simulations of BeF<sub>2</sub> glass, it is observed that a few percent of the ions are capable of displacements of the order of 1 Å in 10 ps at temperatures lower than 300 K. It is shown that these ions are located at well-defined defect sites in the glass. The activation energy for such motion is between 0.03 and 0.2 eV. Ions making large displacements often return to their starting points after a few picoseconds (periodic motion). It is suggested that such mobile ions are responsible for the low-temperature anomalous properties of glass.

PACS numbers: 61.40.Df

Many inorganic glasses have anomalous thermal, acoustic, and dielectric properties at temperatures ranging from a few millidegrees to 100 K.<sup>1</sup> The measured anomalies are of two types. In a number of glasses at temperatures above 10 K, including BeF<sub>2</sub> and silica, there is a broad, strong acoustic absorption associated with activated hopping over potential barriers of height a few hundred to about 1000 K.<sup>1,2</sup> At temperatures below a few degrees Kelvin (where vitreous silica has been studied most extensively), the situation is different. There, the speci-

fic heat, thermal resistance, and negative thermal expansion are all unusually large and have anomalous temperature dependencies. There is considerable saturable acoustic absorption at all frequencies below 35 GHz. Phenomenologically, the excitations producing these very-low-temperature anomalies are two-level systems (TLS) with energy separations ranging from 0 to at least 35 GHz.<sup>3-6</sup>

The experimental results indicate that an atom, or group of atoms, is somehow loosely bound and so moves about relatively freely, presumably