urements[4] have given information about the positions of the various conduction bands. The present work has delineated some of the valence band structure parameters. The phonon energies at the edge of the Brillouin zone have also been measured by observing multiple phonon absorptions in the lattice vibrational spectra.[16] The availability of the above information makes the Ge-Si system a desirable one upon which to test various theoretical models of the band structure of disordered alloys.

ACKNOWLEDGMENTS

The author wishes to acknowledge the contribution of samples for these measurements by S. M. Christian and W. Harty and the crystal growing facilities of the RCA Laboratories. He also gratefully acknowledges the aid of Dean Kramer in obtaining the experimental data and his colleagues at RCA Laboratories for discussions of the nature of the band structure of the Ge-Si alloy system.

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Lattice Vibration Spectra of Germanium-Silicon Alloys[*]

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The infrared lattice absorption spectra of germanium-silicon alloys were determined in the wavelength region from 8–48 μ and have been analyzed to obtain information on the lattice vibrational spectra of the disordered crystals. The evolution of the spectra was followed from pure germanium through the alloys to pure silicon and the major two-phonon combination bands were identified. The optical and acoustical frequencies near the edge of the reduced zone were determined throughout the alloy system by identifying equivalent bands in the alloys with those of pure germanium and silicon which were assigned by using neutron scattering data. The gross features of the spectra revealed a continuous variation of the positions, shapes, and the intensities of the absorption bands as a function of composition; however, the strongest germanium-like summation band $(TA+TO)$ approaches but does not merge with the equivalent silicon-like band. It is possible to observe both of these bands simultaneously on samples near the central range of composition. The appearance of new bands, not present in either pure germanium or pure silicon, due to the addition of small amounts of silicon to germanium or vice versa, were identified as vibrational impurity bands. The relative insensitivity of the phonon energies with composition are in agreement with a previous determination of equivalent phonons involved in the indirect transitions of the intrinsic absorption edge. The results of the analyses of the lattice absorption spectra of germanium-silicon alloys are compared with various theoretical models that have been proposed for the vibrational spectra of disordered crystals.

In this work, the infrared lattice absorption spectra of the germanium-silicon alloys were observed in the spectra region from 8 to 48 μ and were analyzed to obtain information on the lattice vibrational spectra of the disordered crystals. Although considerable experimental information has been accumulated in recent years regarding the vibrational spectra of regular crystals, correspondingly little experimental information is available concerning the vibrational spectra of disordered crystals. The theoretical understanding of the lattice vibrational spectra of regular crystals is sufficiently advanced in the case of germanium and silicon to enable one to calculate the lattice vibration dispersion curves[1,2] which are in agreement with those experimentally determined by neutron scattering.[3–6] The theoretical methods that are employed for regular crystals depend intimately upon the periodicity of the regular lattice and cannot be directly applied to cases where small impurity concentrations are added to the solid or to the case of mixed crystals. It was the intent in undertaking this study of an infrared absorption spectra of a Ge-Si alloys to obtain some information on the vibrational spectra of disordered lattices that may serve as a spur to the theoretical studies of the problem and to serve as a check on future theoretical developments.

The Ge-Si alloy system was selected for study since the infrared lattice absorption spectra of germanium and silicon[7–9] are known in considerable detail and, consequently, one can attempt to understand the spectra of the disordered lattice by reference to the spectra of the pure constituents of the alloys. This alloy system is also well suited for study since its electronic band structure is fairly well delineated both experimen-

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tally[10–13] and theoretically.[14] Some information on the phonon spectra of Ge-Si alloy is also available from the study of the intrinsic optical absorption edge of the alloys, where the phonons assisting in indirect optical transitions were identified throughout the alloy system.[11] Some of the phonons which participate in tunneling in indirect transitions using degenerate junctions were also identified for the Si-rich alloys.[15]

Perhaps the main interest in studying the infrared absorption spectra of germanium and silicon, in recent years, has been the fact that the symmetry of the perfect diamond lattice forbids single phonon absorption of radiation because of a lack of a linear electric moment. Consequently, the absorption is probably due to multiple-phonon processes which allow a second-order electric moment to be induced[16] which provides the coupling to the radiation field. The possibility that some of the absorption bands may be infrared active due to the high isotopic content of germanium and silicon was considered in the past[8]; the role of isotopes in the infrared absorption of germanium and silicon have been recently reconsidered.[17] The Ge-Si alloys bear some resemblance to isotopic substitution and, consequently, could perhaps clarify this point.

Theoretical studies have shown that if a perturbing mass is introduced in an otherwise regular lattice, it is possible for new vibrational frequencies to split off from the normal modes of the regular crystal. Germanium and silicon both have the same valency, and, consequently, no new electronic states are expected to be introduced by the substitution of germanium in a silicon lattice or vice versa. It, consequently, forms an ideal system for the study of the effects of disorder on vibrational spectra and to seek evidence for the formation of vibrational impurity bands.

EXPERIMENTAL—SAMPLES AND APPARATUS

The samples used in these measurements were selected for homogeneity of composition and low free-carrier concentration. Single crystals were used in the composition range 0 to 20% silicon and 90 to 100% silicon in germanium; the intermediate compositions were coarse polycrystals. In the range of composition where both single and polycrystalline samples were available, measurements of the lattice bands yielded identical results justifying the use of polycrystalline samples. The compositions of the samples were determined by x ray means using the lattice constant data of Johnston and Christian[10] and were determined to an accuracy of 1% of the amount present. Samples necessary for the analysis of composition were selected from sections of ingot immediately adjacent to those used for the optical measurements.

In undertaking a study of the lattice absorption spectra of a complete alloy system, it is necessary to have some reasonable assurance that the observed bands are characteristic of intrinsic material and that some of the spectra is not due to some unknown impurities or lattice defects. There is some assurance that the observed spectra in this study are characteristic of the intrinsic material, since spectra obtained with samples prepared by different growth techniques but with approximately the same composition yielded similar results. It was not possible to obtain samples with identical composition from different ingots prepared in a different fashion, because of the very manner of preparation of the samples which yielded a gradient of composition along the length of an ingot. The systematic evolution of the positions and shapes of the observed bands with composition for samples selected from different ingots indicated that most of the observed spectra are characteristic of the intrinsic alloys. The free-carrier concentrations of the samples were as low as possible so as not to obscure the lattice absorption bands by free carrier absorption. In some cases, the crystals were grown with appreciable donor and acceptor compensation to keep the free-carrier concentration low. When the free concentrations were sufficient to contribute to the optical absorption, it was still possible to distinguish the lattice absorption bands superimposed upon the broad free-carrier absorption background.

The optical system used was a Perkin-Elmer single-pass prism monochromator with the sample placed at the exit slit of the instrument. For optimum resolution, CaF_2, NaCl, KBr, and CsI prisms were used in the appropriate wavelength regions. Special care was taken to minimize the effects of scattered light by the use of appropriate restrahlen reflection plates, scatter mirrors, and beam choppers. The monochromator was calibrated by determining the positions of known absorption bands.[18] Analytical expressions for the wavelength calibration curves were fitted to the calibration bands, following the procedures described by McKinney and Friedel.[19]

It was necessary to take rather extensive absorption data to sufficiently delineate the lattice absorption bands throughout the alloy system. Each sample run was equivalent to performing a complete optical absorption experiment on pure germanium or silicon; consequently, some automation of the data processing was undertaken. The exact procedures are described elsewhere.[20] Essentially, the single-beam transmission

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data were converted to percent transmission by use of an analog computor. A program was prepared for the IBM-650 digital computor which contained the analytical expressions for the calibration curves and the equations for obtaining absorption coefficients from the transmission data, with appropriate corrections for multiple reflections. The reflectivity coefficients were determined by measuring the transmission to the long-wavelength side of the absorption edge of intrinsic material for each composition and assuming that the transmission was limited by the reflectivity of the sample.

RESULTS—SPECTRA

The lattice absorption spectra of pure germanium and pure silicon and the alloys are shown in Fig. 1. The spectra for pure germanium[7,8] and silicon[7–9] are similar to those previously reported in the literature. For several atomic percent silicon in germanium or vice versa, the general features of the spectra are similar to the lattice spectra of the dominant constituent, except for slight changes in the position and the shapes of the bands. If one examines the spectra in the central region of composition, it would not be possible, off-hand, to identify the spectra as that due to germanium or silicon. However, if attention is focused on a few prominent bands such as the bands at 300, 343, and 421 cm^{-1} of germanium, it is possible to identify these bands in the alloys by following the slow changes in the position with composition. In a similar manner, it is possible to follow the silicon bands at 610, 741, and 885 cm^{-1} into the alloys. The striking feature of the spectra in the alloys is that up to 10% silicon in the germanium and vice versa, the structure of the optical absorption is distinctly recognizable as that due to germanium or silicon, depending upon which is the dominant constituent.

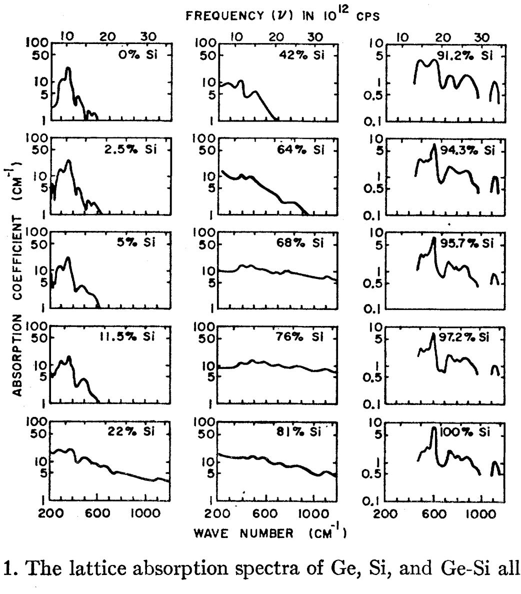

FIG. 1. The lattice absorption spectra of Ge, Si, and Ge-Si alloys.

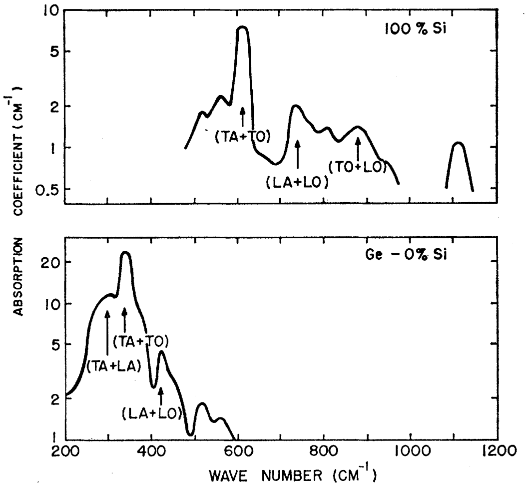

FIG. 2. The lattice absorption spectra of Ge and Si with the assignments of combination bands suggested by the neutron scattering data of Brockhouse and Iyengar (reference 3).

Although there are slight changes in the shapes, positions, and relative intensities of the bands with composition, in general, most of the bands that are present in pure germanium or silicon are still present throughout a wide range of alloy composition.

Aside from the germanium and silicon-like bands present in the alloys, a new band starting at 214 cm^{-1} is formed at the germanium-rich side of the system beginning with an addition of 2.5% silicon to germanium. A band beginning at 508 cm^{-1} is also formed at the silicon end of the alloys when a small amount of germanium is added. Both of these bands grow in intensity and shift slightly with position as the silicon and germanium content is increased.

In Fig. 2, we have plotted the spectra of pure germanium and silicon and have identified the dominant summation bands given by Brockhouse[6] using neutron scattering data.[3] The combination bands due to the sum of the transverse optical and transverse acoustical branches, $(TO+TA)$, the longitudinal optical and longitudinal acoustical branches, $(LO+LA)$, and the transverse optical and longitudinal optical phonons, $(TO+LO)$, are shown for silicon. For germanium, the $(TA+LA)$, $(TA+TO)$, and the $(LA+LO)$ are indicated. These prominent summation bands can be identified in the silicon side and the germanium side of the composition range, respectively. In Fig. 3 and Table I are shown the positions of the two-phonon summation bands in germanium, silicon, and the alloys. The germanium and silicon-like designations used for the bands are by virtue of the identifications made of their positions relative to that of the pure germanium or silicon bands. From Fig. 3 and Table I, it is seen, in general, that there is a slow change in the shapes and the positions of the bands as germanium or silicon are added to the dominant lattice. The bands shift to higher frequencies as the lighter silicon atoms are substituted in

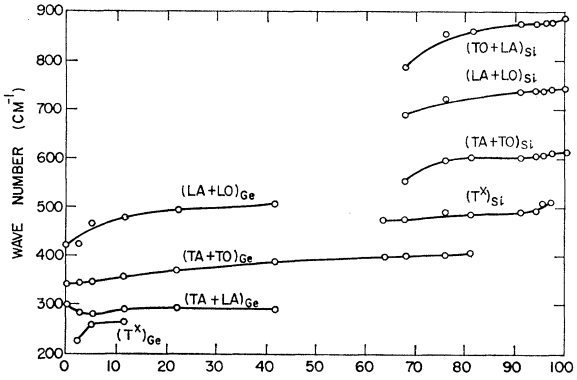

FIG. 3. Some of the two-phonon summation bands in Ge-Si alloys. The subscripts Ge and Si refer to the band assignments made with reference to the pure-Ge or Si spectra.

the lattice, and toward lower frequencies as the heavier germanium atoms are added.

Although the gross features of the spectra reveal a continuous variation of the positions and the intensities of the bands with composition, the germanium-like spectra approach but do not merge with the silicon-like spectra. In fact, it is possible to identify germanium and silicon-like summation bands on samples with 68, 76, and 81% silicon content. The general features spectra in the central range of composition seem to indicate graphically that one is seeing a superposition of pure germanium and silicon lattice absorption bands only slightly perturbed due to the addition of the two constituents. The samples with 22, 68, 76, and 81% silicon in germanium have a background absorption due to free carriers; however, it is still possible to distinguish the lattice absorption peaks riding on this broad background. It should also be noted that the absorption coefficients of the silicon and germanium-like bands decrease as the composition contributing to the respective bands is decreased.

At the germanium end of the alloys, some structure was observed in the region from 800 to 1000 cm^{-1} for pure germanium and up to 11.5% silicon in germanium. These subsidiary peaks correspond to the structures reported by Simeral[8] and were identified as 3-phonon summation bands by Brockhouse.[6] These structures were not plotted in Fig. 1 since the absorption level was too low to give reliable data for the sample thicknesses employed for the measurements. In general, the low absorption coefficients reported in Fig. 1 can have systematic errors of the order of 20%, since the sample thicknesses were between 20 and 40 mils. These thicknesses were dictated by the necessity of having a reasonable homogeneous composition throughout the sample dimensions since there is a continuous variation of the absorption structures with composition. The alloys were prepared in such a fashion that there was a continuous gradient of composition along the length of an ingot, but the above thicknesses gave assurance of a reasonable homogeneity of composition.

The band at 1100 cm^{-1} seen in pure silicon and down to 68% silicon in germanium is the characteristic band due to an oxygen contaminant in the lattice.[21,22] The band is also seen in samples with 22% silicon in germanium because the general background level of absorption has increased by the presence of free carriers. Attempts were made to look for the corresponding oxygen band in germanium due to the Ge-O vibrational band, in the region around 11.5 μ at nitrogen temperatures.[21] However, this band could not be found in pure germanium or the alloys due to the low levels of absorption for this band. The presence of the Si-O band in the alloys up to 22% silicon leads one to infer that most of the oxygen is bonded to silicon rather than germanium in the alloys. This is to be expected because of the greater affinity of oxygen for silicon than germanium. A more careful study of the oxygen band on the silicon-rich end of the system and the search for the analogous band on the germanium side could prove interesting for a study of the kinetics of oxygen bonding in germanium-silicon alloy lattices. The spectra of oxygen contaminated silicon containing 2% germanium have been studied in some detail.[23]

To further study the nature of the new band formed in the alloys at the silicon end of the system, due to the addition of germanium, the absorption spectra of pure silicon and 10% germanium in silicon was measured as

TABLE I. Two-phonon summation bands in Ge-Si alloys.

	Germanium-like		
Mol. % Si	$(TA+LA)$ (cm^{-1})	$(TA+TO)$ (cm^{-1})	$(LA+LO)$ (cm^{-1})
0	300	343	421
2.5	281	346	425
5.0	281	350	469
11.5	292	355	483
22.0	292	371	492
42.0	288	388	510
64.0		394	
68.0		400	
76.0		400	
81.0		406	
	Silicon-like		
Mol. % Si	$(TA+TO)$ (cm^{-1})	$(LA+TO)$ (cm^{-1})	$(TO+LO)$ (cm^{-1})
68.0	558	690	781
76.0	598	723	860
81.0	598	712	850
91.2	598	738	875
94.3	604	738	875
95.7	606	733	871
97.2	609	740	875
100.0	610	741	885

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a function of temperature. These results are shown in Figs. 4 and 5; the summation band ($TA+TO$) at 610 cm^{-1} in Si, and the corresponding band at 589 cm^{-1} in 10% Si, have approximately the same temperature dependence. The new band at 485 cm^{-1} shown in Fig. 5 which is absent in pure silicon also exhibits a temperature dependence similar to that of the 598 cm^{-1} band, i.e., it decreases in intensity as the temperature is decreased. The temperature dependence of the 214 cm^{-1} band at the germanium side of the system which is not present in pure germanium was not run, since the numerical aperture of the optical system used with the Dewar was such that an excessive loss in intensity was suffered making it impossible to make reliable data in the 48-μ region.

We may summarize the observed spectra of Ge-Si alloys shown in Fig. 1 by noting the following salient features of the spectra:

(1) At the germanium- and silicon-rich end of the composition range, the lattice absorption spectra of the alloys resemble the pure spectra of the dominant constituent. As the composition is varied, the positions of the dominant peaks are relatively insensitive to the composition, except for slight changes in their positions, shapes, and heights of the bands. Although the spectra change with composition, it is still possible to identify the summation band ($TO+TA$) characteristic of germanium and silicon on samples with 64, 68, 76, and 81% silicon. The germanium- and silicon-like spectra, therefore, approach each other but do not merge.

(2) Two new bands are formed by alloying germanium with silicon and vice versa. The band at approximately 214 cm^{-1} at the germanium end of the system and the one at approximately 508 cm^{-1} on the silicon end of the system continue to grow in intensity as silicon and germanium, respectively, are added to the lattice. These can be identified as vibrational impurity bands and will be discussed later in the text.

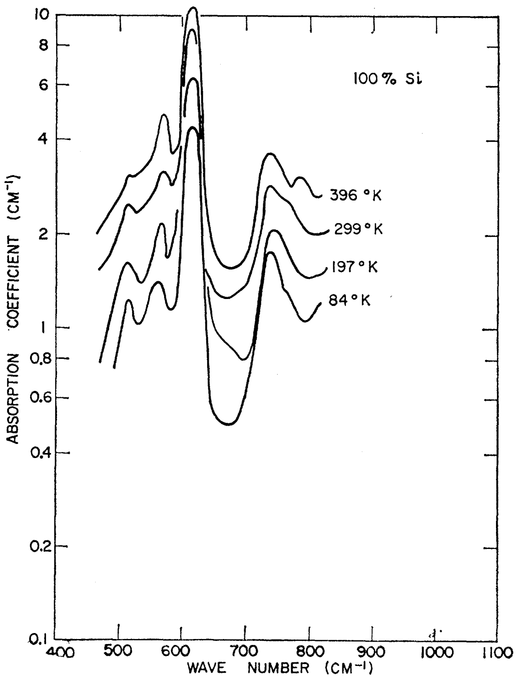

FIG. 4. Lattice absorption in pure-Si as a function of temperature.

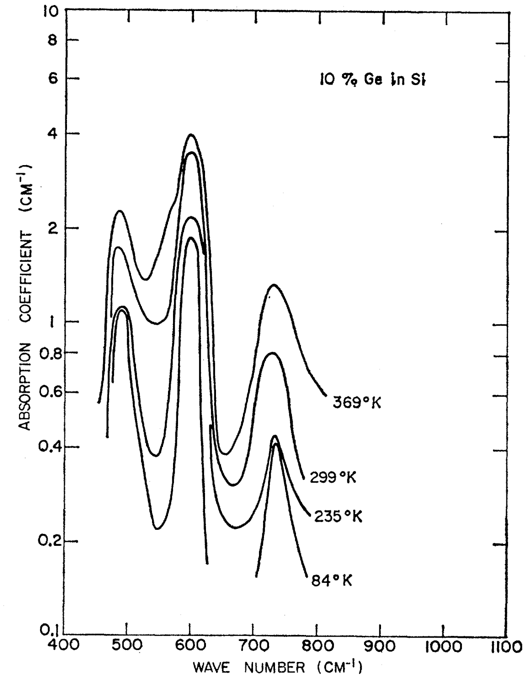

FIG. 5. Lattice absorption in Ge-Si alloy with 10% Ge as a function of temperature.

INTERPRETATION OF THE SPECTRA

Before proceeding with the identification of the lattice spectra of Ge-Si alloys, let us summarize what is known of the infrared lattice absorption spectra of pure germanium and silicon. Germanium and silicon both have a diamond-type lattice and hence, by symmetry, lack a first-order electric moment, and, consequently, radiation cannot interact with the solid by a single-phonon process. The existence of optical absorption in these

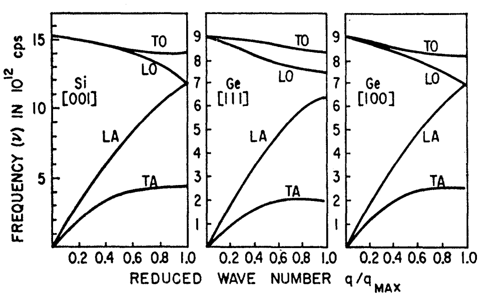

FIG. 6. The vibrational dispersion curves of Ge and Si as determined by neutron scattering. The Ge curves are taken from Brockhouse and Iyengar, (reference 3), while the Si curves are taken from Brockhouse (reference 4). The experimental points are eliminated from the figures.

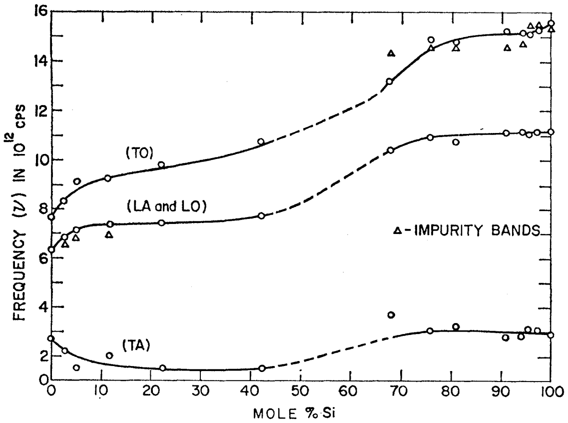

FIG. 7. The phonon frequencies in Ge-Si alloys near the edge of the reduced zone derived from the lattice absorption bands.

crystals has been shown by Lax and Burstein[16] to be due to a second-order process whereby a second-order electric moment can be induced by a two-phonon process. The observed temperature dependence of the absorption in germanium and silicon has been taken as evidence that two-phonon processes are active in the absorption.[7]

Figure 6 shows the vibrational modes of germanium and silicon in some of the principal directions determined by neutron scattering.[3–6] Using the above dispersion curves, it has been shown that a reasonable assignment can be made of the sum and difference bands observed in the infrared lattice absorption spectra of germanium and silicon.[6] If one assumes that the matrix element for the interaction does not depend strongly upon the wave vector of the phonons, the peaks of the lattice absorption spectra can be associated with peaks of the combined densities of states of the appropriate phonon branches. The peaks in the densities of states of the phonon branches are expected to occur near the edge of the reduced zone in germanium and silicon. Consequently, the summation bands give a mapping of the densities of the states of the short-wavelength phonon branches.

In Fig. 2 we have plotted the observed lattice absorption bands for germanium and silicon and have indicated the phonon summation band assignments of the three prominent bands given by Brockhouse.[6] Analogous bands can be identified in the alloys with reference to these peaks and are shown in Fig. 3, where the summation bands identified by subscript Ge and Si are with reference to the identifications made with respect to pure germanium or pure silicon. The band positions indicated by T_{Ge}^* and T_{Si}^* are the new bands which appear at the germanium and silicon rich ends of the system and are not present in the pure constituents. It should again be noted the prominent germanium and silicon summation bands $(TA+TO)$ can be observed simultaneously in the 64, 76, 67, and 81% Si samples.

In Fig. 6 there are four-phonon branches for the indicated symmetry directions. It should be noted that near the edges of the zone in germanium and silicon the LA and the LO frequencies are nearly equal. In the alloys, we have observed three absorption bands which involve 4 unknown phonon energies. If it is assumed that throughout the alloy system the LA phonons are equal to the LO phonons at the edge of the zone; it is possible to solve for the four-phonon frequencies throughout the entire range of composition in the alloy system.

The results of the calculations for the phonon energies are shown in Fig. 7 and Table II. The phonon summation bands $(TA+TO)_{\mathrm{Ge}}$ in the region where they overlap the silicon-like summation bands were eliminated from the above calculations. We see that the TO, LA, LO are relatively insensitive to composition changes at the germanium and the silicon ends of the alloy system. However, the germanium frequencies increase slightly with increased silicon content and the corresponding silicon frequencies decrease with the increased germanium content. The TA frequency seems to initially decrease with increased silicon content on the germanium side of the composition range. However, since the TA frequencies are calculated from differences of rather large numbers, they may contain rather appreciable errors. It should also be emphasized that the above calculations assume that we are dealing with four distinct phonon branches at the edge of the reduced zone, but in fact for any arbitrary direction, six phonon branches are possible and, therefore, the values in Fig. 7 actually represent average phonon frequencies over all crystal directions.

In Fig. 7, the germanium and silicon ends of the alloy system are joined by a dashed curve. This procedure is not entirely correct, since we have previously noted that one can identify the germanium- and silicon-like bands on the same sample in the central range of composition.

TABLE II. The phonon frequencies near the edge of the reduced zone of Ge-Si alloys as derived from the lattice absorption bands. The bands labeled T^x are vibrational impurity bands.

		Germanium-like			
Mol. % Si	TA (cm^{-1})	TO (cm^{-1})	LA (cm^{-1})	LO (cm^{-1})	T^x (cm^{-1})
0	90	254	211	211	
2.5	69	278	213	213	214
5.0	47	303	235	235	229
11.5	51	305	242	242	231
22.0	46	325	246	246	
42.0	33	355	255	255	
		Silicon-like			
Mol. % Si	TA (cm^{-1})	TO (cm^{-1})	LA (cm^{-1})	LO (cm^{-1})	T^x (cm^{-1})
68.0	122	436	345	345	481
76.0	100	498	362	362	487
81.0	104	494	356	356	488
91.0	92	506	369	369	485
94.3	98	506	369	369	488
95.7	102	504	367	367	509
97.2	104	505	370	370	508
100.0	95	515	371	371	

The spectra of the alloys in this central range of composition cannot be considered to be primary germanium-like or silicon-like. It appears as if the vibrational modes of germanium and silicon are both present.

The points indicated in Fig. 7 as impurity bands are the new bands that are not present in pure germanium or silicon but appear when germanium and silicon perturbing masses are added to the lattice. It should be noted that the impurity band of the silicon end of the system coincides within experimental error with the silicon-*TO* frequency, while the impurity band of the germanium end of the system coincides with the germanium *LA* and *LO* frequencies and do not occur at an intermediate frequency. This seems to indicate that the new bands are due to the activation of some of the fundamental lattice modes by the presence of a perturbing mass.

DISCUSSION

At present, there is no adequate theory to account for lattice vibrational spectra of a disordered 3-dimensional alloy. Dyson[24] has given a rigorous solution for the vibrational spectra of the one-dimensional disordered linear chain. Other treatments of the one-dimensional problem have been given by a number of authors whose work has been summarized in a review article.[25] Unfortunately, the physically interesting 3-dimensional problem does not seem to be amenable to these elegant mathematical formalisms. Montroll and Potts[26] have considered the effects of infinitely small concentrations of localized defects on the vibrational spectra of crystals. Domb *et al.*[27] have studied the vibrational frequency spectra of the randomly disordered 2-component isotopic linear chain for wide ranges of concentration and mass ratios. These results indicate that most of the normal modes are only slightly perturbed by the presence of defects, and that defects can cause localized modes of vibration to be displaced out of the frequency bands of the perfect crystal. At high-impurity concentrations, these localized modes broadened into vibrational impurity bands.

Two-Phonon Summation Bands

The observation in the present work that the vibrational spectra at the germanium and silicon ends of the system are insensitive to composition is also indicated by the results of two other independent types of experiments. The phonons participating in nonvertical optical transitions throughout the alloy system were determined by Braunstein, Moore, and Herman[11] in a study of the intrinsic absorption edge. In this work it was shown that the phonons participating in the nonvertical transitions were essentially a weighted average of the *LA* and *TA* phonons. Figure 8 shows the equivalent temperature of phonons participating in these indirect electronic transitions throughout the alloy system. The striking similarity of the *s*-shaped curve observed by this method and the results of the present work shown in Fig. 7 is to be noted. Ando[15] has determined some of the phonons participating in tunneling by measuring the current voltage characteristics of degenerate junctions in the region of composition from 0 to 9.1% germanium in silicon and finds agreement with the above observations.

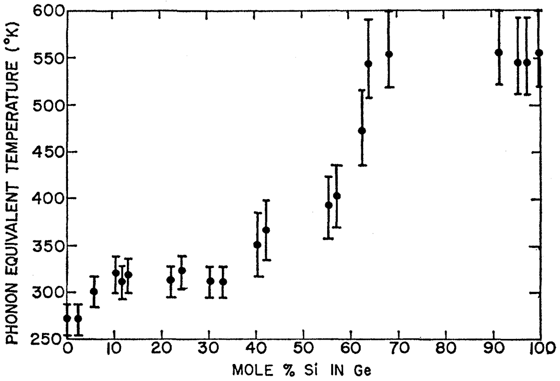

FIG. 8. The characteristic temperature of phonons participating in the nonvertical transitions in Ge-Si alloys as determined by Braunstein, Moore, and Herman (reference 11) from the intrinsic absorption edges.

One attempt to calculate the normal modes of vibration for a 3-dimensional disordered crystal, specifically that of germanium silicon was based on a virtual crystal approximation.[11] According to this model, the disordered crystal was replaced by an equivalent ordered crystal with each lattice site occupied by the same type of hypothetical atom, whose mass was uniquely defined by the composition of the virtual crystal. It was found that the virtual crystal approximation predicts a substantially linear variation with composition of nearly all of the normal modes. The virtual crystal approximation should be a satisfactory approximation for the case of long-wavelength acoustic modes since many lattice sites are involved and the specific arrangements of atoms should not be of prime importance. However, one should expect this model to fail for the short-wavelength modes which have been determined in the present work, since here the local distribution of atoms is germane to the problem.

Another model which was used in an attempt to calculate the vibrational spectra of the Ge-Si alloys was to simulate the alloy system by a series of ordered crystals formed by germanium and silicon, arranged in different ways among the lattice sites.[11] This model essentially introduced short-range order into the problem, though there is no evidence for any order in these alloys. The ordered crystal model predicted 4 types of behavior for the normal modes, none of which are linear

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with composition. One type of behavior resembled the experimental results for the variation of normal modes with composition, but there is no *a priori* reason why this should be the correct one.

The spectra in the central range of composition shown in Fig. 1 are distinguished from the other compositions by the fact that one can observe germanium- and silicon-like bands on the same sample. To first order, it appears as if the lattice vibrational spectra of Ge-Si alloys are a superposition of pure germanium and silicon. One may explain these results by assuming that the alloys consist of an appreciable clustering or precipitates of a reasonable number of atoms. The short-wavelength vibrations of the alloys which are responsible for the combination bands would be selected from the localized modes of vibration of the germanium and silicon aggregates. In general, the transport properties, such as the mobilities and the specific heats, which are determined by the long-wavelength acoustical modes would be insensitive to localized fluctuations in composition but would be determined by the average composition of the crystal.

Vibrational Impurity Bands

When impurity atoms are introduced into an otherwise perfect lattice, absorption bands, normally forbidden by the selection rules for optical absorption, may be induced by the presence of the perturbing masses. Lax and Burstein[16] have shown that one effect could be to modify the electronic structure in the immediate vicinity of the impurity so as to induce a linear electric moment which could couple to the radiation field by a single-phonon absorption. It has been suggested that a specimen dependent absorption in type-I diamond is due to this type of coupling mechanism.[16] Kaiser and Bond[28] have shown that the bands in type-I diamond may be associated with the presence of nitrogen impurities in this lattice. The activation of single-phonon infrared lattice absorption in diamond by neutron radiation was observed by Smith and Hardy.[29] They further proposed that the common features of the neutron-activated absorption and the absorption in type-I diamond suggests a similar origin for both types of absorption and are not necessarily due to C-N vibrations.

Since germanium and silicon have a common valency, it is not expected that any new electronic states would be introduced by the substitution of either one as an impurity in the lattice of the other. Consequently, crystal symmetry would still forbid the formation of a linear electric moment. However, Lax and Burstein[16] have shown that in this case the magnitude and character of the vibration in the immediate vicinity of an isotope could change with the consequence that a pair of modes which do not normally absorb radiation may now have an appreciable absorption near the impurity. Thus, although an impurity-induced linear moment will still be forbidden in this case, a second-order moment is possible which could lead to combination band absorption at a frequency near the maxima in the density of states of the normal modes. One would in turn expect a temperature-dependent absorption for this type of impurity band. While in the case of an impurity band induced by a linear moment, the absorption would be temperature independent.

As we have seen, the impurity band at 485 cm^{-1} shown in Fig. 5, introduced in the predominantly silicon lattice by the presence of germanium, occurs at *TO* of silicon and has a temperature dependent absorption which is similar to that of the summation band $(TA+TO)$ in pure silicon. On the germanium side of the alloy system, the new band at 214 cm^{-1} which appears when the silicon is added to an otherwise dominant germanium lattice, occurs at the *LA* frequency of germanium. The temperature dependence of the 485 cm^{-1} band indicates that it is likely a vibrational impurity due to a second-order moment of the type discussed by Lax and Burstein.[16] The 214 cm^{-1} band is probably of the same origin.

It should be noted that these impurity bands cannot be regarded as due to a purely localized mode of vibration of the Si-Ge bond but may be thought of as an impurity-induced resonance, i.e., a quasistationary impurity level sitting in the allowed band of the host crystal. The peaks of these bands occur within the band of allowed lattice frequencies for the *TO* frequencies of silicon and the *LA* frequencies of germanium, and, consequently, radiation absorbed at these frequencies must propagate throughout the crystal and these modes must be properly considered to form part of the normal vibrational modes of the entire crystal. This is in contrast to the case of the Si-O vibrational frequencies observed in the alloys and pure silicon which occur above the highest allowed frequency of the lattice vibrational modes and, consequently, can be considered as purely local molecular vibrations. The fact that the Si-O frequency is independent of composition in the alloys further emphasizes the localized nature of these vibrations.

Fan and Ramdas[30] have shown that an absorption band is induced in silicon at 20.5 μ by neutron irradiation which is presumably associated with vacancy and interstitial defects. The position of this peak is close to the *TO* frequency of silicon. They report that this band is relatively temperature-independent and, consequently, is likely due to a single-phonon absorption band. This is to be contrasted with our observation that the band formed at this frequency by the substitution of germanium in silicon is temperature-dependent. Neutron damage may introduce new electronic states which have a linear electric moment. Consequently, absorption near the *TO* frequency could be induced by a first order moment in case of damage defects and in

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the case of germanium-silicon alloys by a second electric-order moment.

We have seen that in the alloys, a silicon impurity activates the *LO* frequency of germanium and that a germanium impurity activates the *TO* frequency of silicon. It should be noted in this respect that in the case of neutron-activated impurity bands in diamond it appears as if the *LO* modes are coupled to the radiation field while there is no evidence from the coupling of the transverse optical modes *TO*.[29]

CONCLUSIONS

The optical and acoustical frequencies near the edge of the reduced zone were determined throughout the alloy system by identifying the major two-phonon combination bands of the alloys with those of pure germanium and silicon by using the phonon assignments given by neutron scattering data for pure germanium and silicon.[6] The variation of phonon energies with composition are in agreement with a previous determination of equivalent phonons involved in indirect optical transitions. Some of the phonons energies that were measured in tunneling in degenerate junctions in silicon-rich alloys[15] are also indicative of the relative insensitivity of phonon frequencies with composition. The composition independence of the phonon energies in the Ge-Si alloys cannot be accounted for by present theories of disordered crystals. The gross features of the spectra suggest that clustering of germanium and silicon atoms may exist throughout the alloy system, and, consequently, the vibrational modes are characteristic of pure germanium and silicon aggregates.

The appearance of new bands not present in either pure germanium or pure silicon, due to the addition of small amounts of silicon to germanium or vice versa, were identified as vibrational impurity bands induced by two-phonon processes. In order to understand further the nature of these impurity bands, it would be of interest to see if these bands are formed at germanium and silicon concentrations of $\ll 1\%$ and to study the temperature dependence of these bands. It would also be of interest to substitute small amounts of lead and tin as impurities in the germanium lattice. Since these are column IV impurities they should play the same role as do germanium and silicon in forming vibrational impurity bands in the alloys. It would also be of interest to look for vibrational impurity bands due to the substitution of donor and acceptor impurities in germanium and in silicon since these do introduce new electronic states and, consequently, can have a linear moment.

Now that three independent techniques have given some information about the vibrational spectra of the disordered alloys of germanium silicon, perhaps these results can motivate further theoretical studies of the three-dimensional disorder problem. The relative insensitivity of lattice absorption bands with changing alloy composition have also been observed in the InP-InAs system.[31] The present experimental work can serve as a check of the correctness of the theoretical models. The determination of the lattice dispersion curves of these alloys by neutron scattering would be of extreme interest in understanding the nature of vibrational spectra of disordered alloys. The Ge-Si alloy system forms an excellent prototype semiconducting alloy system for the studies of lattice dynamics of a disordered lattice.

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