

## Low-Temperature Far-Infrared Spectra of Germanium and Silicon\*

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New high-resolution low-temperature (7.5°K) far-infrared data on intrinsic germanium and silicon are presented. The findings further substantiate the naturally anticipated similarities in band patterns of the vibrational spectra of diamond-type crystals. The low-temperature spectra of germanium and silicon show clearly resolved splits in their principal absorption bands analogous to the intriguing doublet in the band at about 2000 cm<sup>-1</sup> in diamond. A possible explanation is indicated. The room-temperature far-infrared refractive index of both germanium and silicon and the 7.5°K refractive index of germanium have been measured by means of interference fringes.

### 1. INTRODUCTION

THE properties of the group IV elements, diamond, silicon, and germanium, have been extensively studied. This is particularly true of their optical characteristics. Intensive studies on the infrared spectra of diamond were first carried out by Robertson, Fox, and Martin<sup>1</sup> who established the well-known classification into types I and II. Type I diamonds exhibit both long- and short-wavelength absorption bands, while type II absorb only at short wavelengths at positions identical to those of type I. Further measurements<sup>2-7</sup> verified these observations and established the spectral temperature dependence. Measurements on silicon<sup>3,4,8-10</sup> and germanium<sup>3,4,9-13</sup> also abound. It is the purpose of this communication to present some new far-infrared data which were obtained in an attempt to investigate further the problems that still surround the group IV elements.

### 2. EXPERIMENTAL

The far-infrared data have been obtained on a Perkin-Elmer 201-C far-infrared spectrometer that has been modified to cover the range 675-50 cm<sup>-1</sup> in both reflection and transmission and is adapted for liquid-helium temperature range work involving a Hofman research Dewar. The basic techniques used are similar to those described by Lord and McCubbin.<sup>14</sup>

Our data were obtained either by subtraction of results for two different thicknesses of our crystals assuming cancellation of reflection losses or by subtraction of known reflection losses from transmission data. Runs were made on germanium and silicon samples approximately 0.5, 1, and 2 mm thick, which were highly polished on both sides and cut perpendicular to the [111] axis. The low temperature spectra were recorded at 7.5±0.5°K as measured by a carbon composition resistor.

### 3. RESULTS

From structural considerations, it appears that similarities should be found between silicon and germanium, on the one hand, and type II diamond, on the other hand. The spectra of the intrinsic materials in general show similar temperature dependence<sup>3</sup> and relative band intensities follow similar patterns (see Fig. 1).

Especially intriguing here is the clearly indicated split in the band at about 2000 cm<sup>-1</sup> in diamond for which no definite analog had so far been found in either germanium or silicon. When, however, measurements were made on germanium under conditions of somewhat greater resolution than previously reported,<sup>3</sup> we observed a splitting of the most intense band at 347 cm<sup>-1</sup>. When such measurements were made at very low temperatures, definite sharpenings and high-frequency shifts could be clearly observed. In one spectrum a third

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<sup>1</sup> R. R. Robertson, J. J. Fox, and A. E. Martin, *Trans. Roy. Soc. (London)* **A232**, 463 (1934).

<sup>2</sup> G. B. B. M. Sutherland, D. E. Blackwell, and W. G. Simeral, *Nature* **174**, 901 (1954).

<sup>3</sup> R. J. Collins and H. Y. Fan, *Phys. Rev.* **86**, 648 (1952); **93**, 674 (1954).

<sup>4</sup> M. Lax and E. Burstein, *Phys. Rev.* **97**, 39 (1955).

<sup>5</sup> G. B. B. M. Sutherland and H. A. Willis, *Trans. Faraday Soc.* **41**, 289 (1945).

<sup>6</sup> K. R. Ramanathan, *Proc. Indian Acad. Sci.* **A24**, 150 (1946).

<sup>7</sup> H. J. Lipson, U. S. Air Force Cambridge Research Laboratories (private communication).

<sup>8</sup> F. A. Johnson, *Proc. Phys. Soc. (London)* **73**, 265 (1959).

<sup>9</sup> R. C. Lord, *Phys. Rev.* **85**, 140 (1952).

<sup>10</sup> E. Burstein and J. J. Oberly, *Phys. Rev.* **78**, 642 (1950).

<sup>11</sup> H. B. Briggs, *J. Opt. Soc. Am.* **42**, 686 (1952).

<sup>12</sup> I. M. Mills and B. Crawford, Jr., *J. Opt. Soc. Am.* **45**, 489 (1955).

<sup>13</sup> W. C. Price and G. R. Wilkinson, *Molecular and Solid State Spectroscopy Report 1959-1960*, U. S. Army, Contract DA-91-591-EUC-1308 OI-4201-60 (R&D 260) (unpublished).

<sup>14</sup> R. C. Lord and T. K. McCubbin, Jr., *J. Opt. Soc. Am.* **47**, 689 (1957).

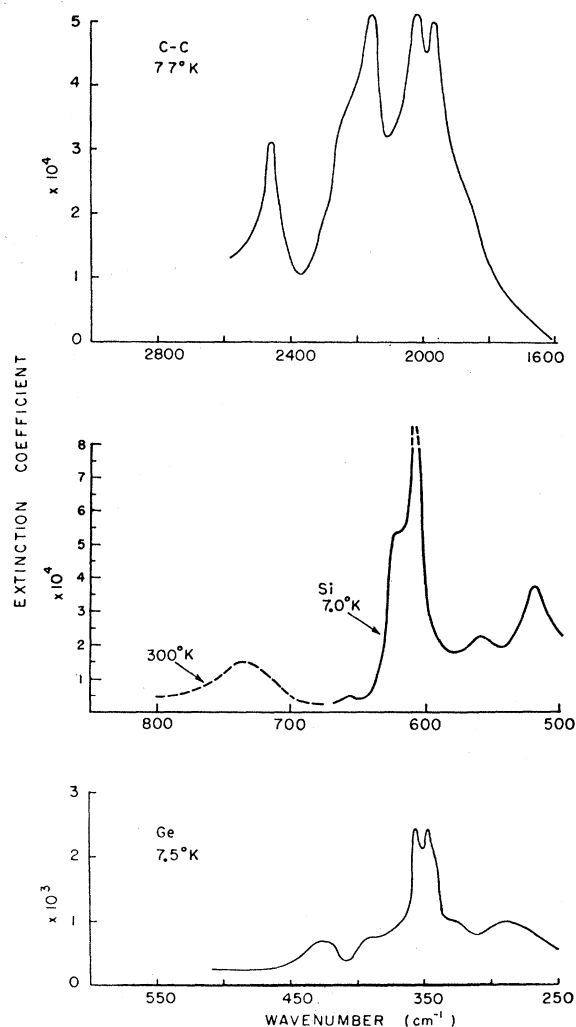


FIG. 1. The infrared spectra of diamond (Ref. 7), silicon, and germanium.

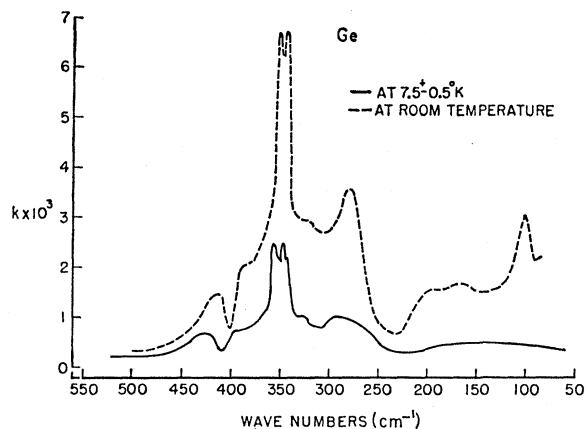


FIG. 2. The far infrared spectrum of germanium at 300 and 7.5°K.

band was marginally observed on a particularly low noise run at these temperatures and it is shown as the  $343\text{ cm}^{-1}$  shoulder in Fig. 2. These findings stimulated a search for similar features in silicon which indeed showed a definite side band.

The absorption at  $100\text{ cm}^{-1}$  in germanium has been ascribed<sup>15</sup> to impurities in the lattice. Because of this, we made additional measurements on very pure samples manufactured by Knapic Electrophysics, Inc., of Palo Alto, California. These samples are claimed by the manufacturer to have about  $1.5 \times 10^{14}$  impurity atoms/cc. The resistivity of this *p*-type material is 50 to 56  $\Omega\text{ cm}$ . The results shown in Fig. 2 seem to indicate that impurities are not the cause of this absorption.

By means of interference fringes, we have measured the far-infrared refractive index of both germanium and silicon at room temperature and the  $7.5^\circ\text{K}$  refractive index of germanium. The constancy of our fringe spacing over the very small peaks in this region

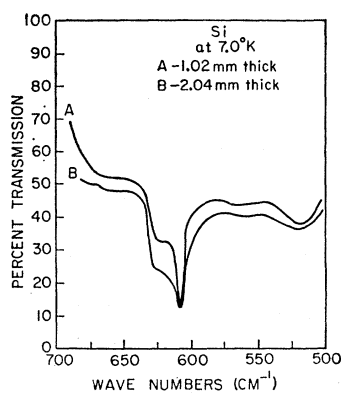


FIG. 3. Infrared absorption of silicon at  $7.5^\circ\text{K}$ .

seems to indicate that there is essentially no refractive index change due to the absorption and so we felt justified in using the simple relationship:

$$n = 1/(2t\Delta\nu),$$

where  $t$  is the crystal thickness and  $\Delta\nu$  is the fringe spacing.

Our results for germanium at  $7.5^\circ$  are  $n = 3.98 \pm 0.02$  between  $150\text{ cm}^{-1}$  and  $225\text{ cm}^{-1}$  and  $n = 3.90 \pm 0.02$  between  $250\text{ cm}^{-1}$  and  $425\text{ cm}^{-1}$ . At room temperature, we obtain  $n = 3.98 \pm 0.02$  between  $70\text{ cm}^{-1}$  and  $120\text{ cm}^{-1}$ . For silicon we obtained  $n = 3.41 \pm 0.03$  between  $50\text{ cm}^{-1}$  and  $90\text{ cm}^{-1}$  and between  $345\text{ cm}^{-1}$  and  $385\text{ cm}^{-1}$ . These values are in reasonable agreement with an extrapolation of Simon's work<sup>16</sup> considering the scatter in his data.

<sup>15</sup> A. Hadni, Spectrochim. Acta 19, 793 (1963); Compt. Rend. 255, 1595 (1962).

<sup>16</sup> I. Simon, J. Opt. Soc. Am. 41, 730 (1951).

TABLE I. Experimental and assigned frequencies for diamond, silicon, and germanium.

Observed Lipson, <sup>b</sup> Lax <i>et al.</i> <sup>c</sup>	Diamond		Observed <sup>a</sup>	Silicon		Observed <sup>a</sup>	Germanium	
	Calculated			Calculated			Calculated	
	Simeral <sup>d</sup>	Raman <sup>e</sup>		Johnson <sup>f</sup>	Simeral <sup>d</sup>		Brockhouse <sup>g</sup>	Simeral <sup>d</sup>
2460			875			418		
2160			730			385		
2020					654, $\omega_1$			356, $\omega_1$
1970			650			350		
1390					625, $\omega_2$	343		
		1332, $\nu_1$	625					341, $\omega_2$
	1326, $\omega_1$		610			325		
	1326, $\omega_2$		570				300, O	
1280	1285, $\omega_3$		515		520, $\omega_3$	280	280, TO	284, $\omega_3$
		1250, $\nu_2$		484, TO			275, TO	
		1239, $\nu_3$			444, $\omega_4$		247, LO	
1190				414, LO				241, $\omega_4$
	1180, $\omega_3$			336, LA				
		1149, $\nu_4$		325, LA				
		1088, $\nu_5, \nu_6$			281, $\omega_5$	195		
1010	1080, $\omega_4$				230, $\omega_5$	165		
		1008, $\nu_7$	165		230, $\omega_6$			153, $\omega_5$
	930, $\omega_4$			152, TA				126, $\omega_5$
		740, $\nu_8$		142, TA		100		126, $\omega_6$
	736, $\omega_5$			139, TA			82, TA	
	700, $\omega_6$			138, TA				67, $\omega_5$
	680, $\omega_4$			128, TA				67, $\omega_6$
		621, $\nu_9$			122, $\omega_5$		65, TA	
	570, $\omega_5$				122, $\omega_6$			
	525, $\omega_6$							
	370, $\omega_4$							
	330, $\omega_5$							

<sup>a</sup> Present paper, room-temperature data.

<sup>b</sup> Reference 7.

<sup>c</sup> Reference 4.

<sup>d</sup> Reference 18.

<sup>e</sup> C. V. Raman, Proc. Indian Acad. Sci. **A44**, 99 (1956).

<sup>f</sup> Reference 8.

<sup>g</sup> Reference 19.

#### 4. DISCUSSION

There has been some dispute in the literature<sup>7,17,18</sup> on the origin of the observed spectra of diamond, silicon, and germanium. The creation of second-order electric moments in multiple phonon processes<sup>4</sup> and impurity induced dipoles<sup>18</sup> have both been suggested as the essential mechanism of absorption.

Various theories and approaches have led to the assignment schemes for all three elements which are brought together in Table I. There is a crucial difference between these assignments. In the first approach, the principal absorption bands are regarded as combination tones,<sup>4</sup> while the other assignment is that of fundamentals.<sup>18</sup>

In connection with the former approach, that of absorptions due to combination tones involving multiple phonon processes, we note that combination modes could account for the doublets in both germanium and silicon using the data of Brockhouse<sup>19</sup> and Johnson,<sup>8</sup> respectively:

<sup>17</sup> G. B. B. M. Sutherland, J. Opt. Soc. Am. **50**, 1201 (1960).

<sup>18</sup> W. G. Simeral, Ph.D. thesis, University of Michigan, Ann Arbor, Michigan, 1953 (unpublished).

<sup>19</sup> B. N. Brockhouse, Phys. Chem. Solids **8**, 400 (1959).

	Observed band (cm <sup>-1</sup> ) (room temperature)	Assignment	
		TO	TA
Germanium	343	276+ 65 = (341)	
	350	280+ 65 = (345)	276+ 82 = (358)
Silicon	610	484+128 = (612)	
	625	484+138 = (622)	

For purposes of comparison, we have compiled in Table II several of the observed frequencies and their ratios for all three elements. Ignoring for the moment

TABLE II. Observed frequencies and their ratios for diamond, silicon, and germanium.

Diamond-Silicon								Charact. temp. (°K)	Ratio
$\nu_A$	Ratio	$\nu_B$	Ratio	$\nu_C$	Ratio	$\nu_D$	Ratio		
1970	3.2	2020	3.2	2160	3.3	2460	3.4	2240	3.5
610		625		650		730		645	
Silicon-Germanium									
610	1.78	625	1.79	650	1.69	730	1.75	645	1.72
343		350		385		418		375	

anharmonic effects<sup>20</sup> these ratios should be of the same order as the ratios of their respective characteristic frequencies  $\nu_{\Theta} \propto (f/m)^{1/2}$  which, as Table II shows, is indeed the case. Figure 1 illustrates the similarities involved in these ratios.

An explanation of the observed splitting as due to an isotope effect could possibly be justified for germanium on the basis of its stable isotope abundance. This explanation, however, clearly must fail for silicon and diamond because suitable stable isotopes are not present in sufficient abundance for these elements.

We have observed an appreciable shift of all bands to higher frequencies with accompanying decrease in the

extinction coefficient on going to low temperatures, as is common for covalent materials.

It is interesting to note that the extrapolation of the absorption versus temperature curves to  $T=0^{\circ}\text{K}$  show positive intercepts, which is in accord with the approach of Lax and Burstein.<sup>4</sup>

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<sup>20</sup> J. N. Plendl, Phys. Rev. **123**, 1172 (1961).

## Saturation Magnetoresistance and Impurity Scattering Anisotropy in *n*-Type Silicon\*

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In the classical strong-field region the magnetoresistance of semiconductors is expected to saturate. If one investigates the dependence of the saturation magnetoresistance upon impurity concentration, i.e., upon the strength of ionized-impurity scattering, quantitative conclusions may be drawn concerning the anisotropy of the relaxation time for such scattering. The strong-field longitudinal magnetoresistance and carrier mobility of phosphorus-doped silicon have been studied in dc magnetic fields to 90 kG at 78°K. Measurements were made on a series of [111]-oriented samples covering the doping range  $2 \times 10^{13}$ – $6 \times 10^{16}$  phosphorus atoms/cm<sup>3</sup>. A quantitative analysis has been made involving Maxwellian averages over carrier energy and relaxation times that combine the impurity, intravalley, and intervalley scattering mechanisms. The strength of the impurity scattering in each sample was taken to be  $\mu_L/\mu$  where  $\mu_L$  is the known lattice scattering mobility and  $\mu$  is the conductivity mobility determined from the measured value of  $R_{\infty}/\rho$ , the ratio of the strong field Hall coefficient to the resistivity. The data agree very well with the theory of Samoilovich, Korenblit, and Dakhovskii (SKD). In the more heavily doped samples, above  $10^{16}$  phosphorus atoms/cm<sup>3</sup>, the effects of neutral impurity scattering are observed.

### I. INTRODUCTION

THE electrical properties of a semiconductor are governed by the electronic energy band structure and by the various processes which scatter the electrons. In the semiconductors which have been most extensively studied, such as silicon and germanium, a detailed picture of the energy bands has been obtained and the major scattering mechanisms have been defined. However, our knowledge regarding the scattering strengths

and anisotropies is more limited. This is partially due to the fact that galvanomagnetic effects such as magnetoresistance, while sensitive to the type of scattering, involve complicated averages over relaxation times of the carrier when measured in normal laboratory magnetic fields. The magnetoresistance has therefore been used primarily to identify the directions of energy extrema in *k* space and to find ratios of the components of the effective mass tensor. The situation is very much altered in the classical strong-field limit.

One of the distinctive features of the galvanomagnetic properties of semiconductors in the classical strong-field region is saturation of the magnetoresistance and Hall

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