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Infrared Lattice Absorption Bands in Germanium, Silicon, and Diamond*

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Infrared absorption bands characteristic of the crystal lattice were investigated for germanium and silicon. The absorption was found to be insensitive to lattice imperfections due to impurities ($\sim 10^{18}$ cm^{-3}) and due to disorders ($\sim 10^{19}$ cm^{-3}) produced by nucleon irradiation. It did vary with temperature in the same way as the calculated mean-square displacement of the atoms. Variations of absorption with temperature were also studied for two specimens of type I diamond. The bands characteristic of type II diamonds showed similar temperature dependence, whereas the long-wavelength bands were temperature insensitive. It appears that the observed absorption in germanium and silicon corresponds to the absorption characteristic of type II diamond and is made possible by the thermal vibration of the atoms. The long-wavelength bands in type I diamonds may be due to impurities.

INFRARED absorption bands in silicon and germanium, which are characteristic of the crystal lattice, were reported independently by the authors[1] and Lord.[2] Previous to these reports Oberly and Burstein,[3] and Briggs[4] have observed an absorption band in high-resistivity silicon at 8.9 microns and ascribed it to the lattice. Subsequently Fan and Becker[5] had shown that this band is in fact characteristic of the silicon lattice, being present in the same strength in all samples. On extending the measurement to 40 microns a number of such bands were found.

Both germanium and silicon have diamond type lattice. Infrared absorption in diamond reported first by Robertson, Fox, and Martin[6] has received considerable attention and has caused controversy in its explanation. A reasonable suggestion[7] is that the absorption is due to lattice imperfections either chemical or physical, but no explanation has yet been established. Aside from the question of availability diamond specimens, being natural crystals, have impurity contents which cannot be controlled. With the modern techniques developed for the preparation of silicon and germanium, it is comparatively easy to obtain large single crystals of known and controllable impurity content. An investigation of the effect of different factors on the lattice absorption in these crystals should contribute to the understanding of absorption in diamond type lattices.

EXPERIMENTAL RESULTS

The absorption studies were carried out on two instruments; a Perkin-Elmer double-pass monochromator which was used for all measurements above 77°K and a Leiss monochromator used for the measurements at 5°K. The cryostat used for the 5°K measurements had polyethylene windows and made measurements from 750–650 cm^{-1} impossible. Furthermore the aperture of the cryostat was small and the accompanying decrease in signal as well as resolution could easily have resulted in an error in the 5°K data of as large as 20 percent. The results obtained are summarized in the following.

(A) The lattice absorption bands of germanium and silicon are shown in Fig. 1. Besides these bands there is absorption due to free carriers, which is proportional to the carrier concentration. These curves are taken on samples with sufficiently small carrier concentration, so

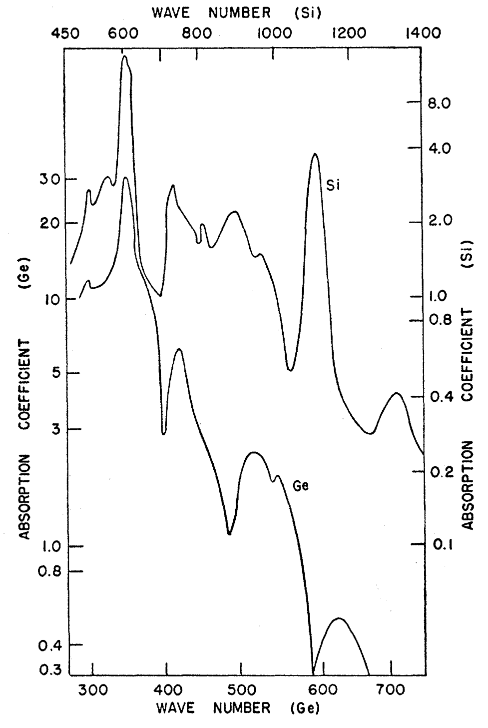

FIG. 1. Lattice absorption in germanium and silicon.

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[1] R. J. Collins and H. Y. Fan, Phys. Rev. **86**, 648 (1952).

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[5] H. Y. Fan and M. Becker, *Proceedings of Reading Conference* (Butterworths Scientific Publications, London, 1951).

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that carrier absorption is negligible. For samples with large carrier concentration, the carrier absorption is superimposed on the lattice bands. When separated the latter are found to be the same in all samples measured. The frequency scale for the germanium curve is 0.56 times that for the silicon. This ratio of the scales is chosen to make the strongest bands for the two materials coincide. It is seen that the band structures for the two substances have considerable similarity.

(B) Impurity and lattice defects. The introduction of impurities affect the carrier concentration of semiconductors. For accurate measurements of lattice absorption the carrier concentration must be kept low. Using donor and acceptor impurities together, large amounts of impurities can be introduced while the carrier concentration remains small. A germanium specimen was cut from such a melt doped with indium and antimony to an impurity concentration of about 10^{18} cm^{-3}. The resistivity of the sample was about 2 ohm cm which corresponds to a small enough carrier concentration to give negligible absorption. The lattice absorption of this sample is the same as that of purest samples with impurity concentration $\sim 10^{14}$ cm^{-3}. Although the purest samples may have more impurities than is indicated by the electrical properties, an addition of 10^{18} cm^{-3} should appreciably affect the total impurity content.

In an attempt to introduce lattice defects a germanium sample was heated to 900°C and rapidly quenched.[8] This treatment did not change the lattice absorption. It has been shown by Gallagher that at temperatures above 500°C germanium may be plastically deformed with slip lines in 111 planes.[9] A specimen was heated to 550°C and subjected to a load producing a 5° bend. The dislocations introduced by this process had no effect on the lattice absorption.

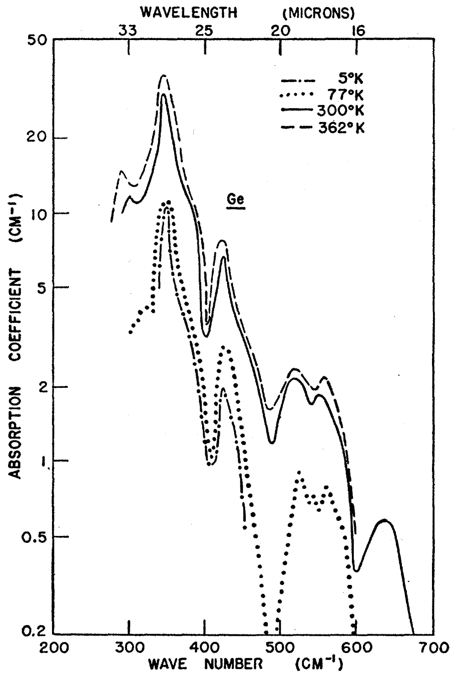

FIG. 2. Lattice absorption in germanium at different temperatures.

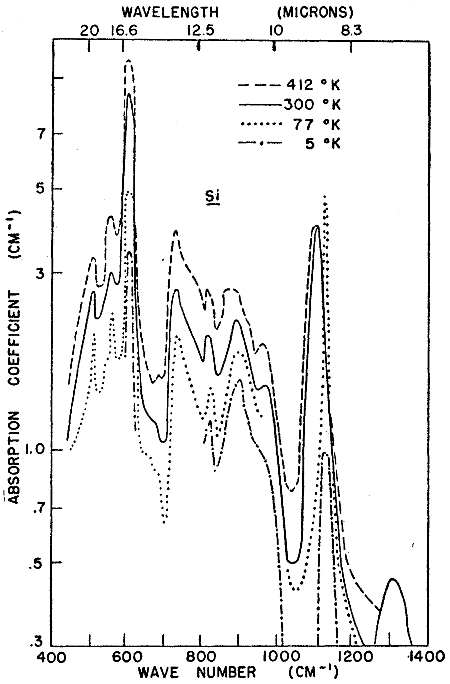

FIG. 3. Lattice absorption in silicon at different temperatures.

It has been reported that, upon irradiation with high-energy nucleons, the resistivity of silicon increases and may reach very high values not obtainable otherwise.[10] Large carrier concentration and high carrier absorption associated with large impurity content can thus be made negligible by nucleon irradiation, making it possible to study the lattice absorption. *P*-type silicon samples of 0.03-ohm cm resistivity with an impurity concentration about 3×10^{18} cm^{-3} were bombarded in the Oak Ridge pile until the resistivity had increased to over 10^3 ohm cm. From Hall effect and resistivity measurements it was estimated that about 10^{19} cm^{-3} lattice defects were produced. These specimens with high concentrations of impurities and lattice defects gave the same lattice absorption as the purest silicon samples.

(C) Temperature dependence. The effect of temperature on the lattice absorption was determined for germanium and silicon from 5°K to 400°K. For temperatures above 400°K the absorption of the thermally excited carriers was too large for the lattice absorption to be studied reliably.

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[9] C. G. Gallagher, Phys. Rev. **88**, 721 (1952).

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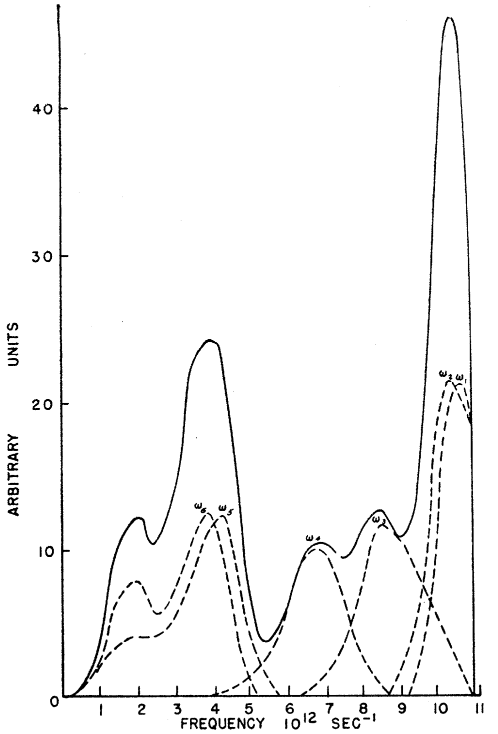

FIG. 4. Frequency distribution of the vibrational modes for germanium calculated by Y. S. Hsieh.

In germanium the lattice absorption increases with increasing temperature (Fig. 2). Within the experimental error all the bands change in the same manner.

For silicon (Fig. 3) except for the 1110 cm^{-1} band the absorption increases with increasing temperature. The exceptional behavior of the 1110 cm^{-1} band as shown by the 77°K curve has been carefully checked. However, at 5°K the band could have sharpened still more but not observed due to insufficient resolution of our equipment. The 1110 cm^{-1} band was the only band in either germanium or silicon which with our resolution showed a clear shift of the peak with temperature.

DISCUSSION

Born's work on the diamond-type lattice based on the interaction of first neighbors was extended by Nagendra Nath[11] to include second-neighbor interactions. The following relation was derived

$$\frac{(8\times 4\pi^2c^2m\nu_0^2/a)[4\pi^2c^2m\nu_0^2/a+8c_{11}-16c_{44}]}{[3\times 4\pi^2c^2m\nu_0^2/a-8c_{11}+16c_{12}]^2}=1, \quad (1)$$

where ν_0 is the limiting frequency of vibration, $2a$ is the lattice constant, m is the atomic mass, c is the velocity of light, and c_{11}, c_{12}, c_{44} are the elastic constants. The values of the constants are given in Table I. Using the frequency ν_1 of the strongest absorption peak for ν_0, the calculated values of the ratio in (1) come out close to unity (fifth row, Table I). This seems to indicate that the strongest absorption band corresponds to the excitation of optical modes of vibration. However, in the case of diamond ν_0 is known from the frequency shift of the first-order Raman line to be $\nu_0=1332$ cm^{-1}. Using this value, the ratio in (1) is 1.40 (Table I), rather poor agreement. Born[12] has pointed out three possible explanations for this discrepancy: (a) interaction of more distant neighbors is appreciable, (b) second-neighbor forces are not central as assumed in (1), (c) experimental error in the values of elastic constants. The relation (1) loses its validity if (a) and (b) are true. On the other hand, in her calculations for diamond Smith[13] adjusted the value of c_{44} from the experimental value 4.3×10^{12} to 5.0×10^{12} dynes/cm^2, which gives 1.04 for the ratio in (1).

The various bands in the absorption might correspond to the excitation of combination modes.[14] Calculations for germanium have been made by Hsieh[15] following Smith's[13] method but using only first-neighbor interaction. The calculated frequency distribution of vibrational modes is given in Fig. 4. The curve is a composite of three acoustical branches (dotted curves 1, 2, and 3) and three optical branches (4, 5, and 6). Any two modes with wave-number vectors equal and opposite in sign, for example one optical and one acoustical mode, could be excited if they are not forbidden by other selection rules. Thus a continuous absorption with various peaks could be expected. However, the quantitative reliability of the calculation is questionable and the relative intensities expected for the excitation of various combinations has not yet been worked out. Therefore it is not yet possible to elaborate on the explanation of the observed spectrum.

The results on the temperature dependence gives an important clue for the understanding of the absorption. According to the symmetry of the diamond lattice, optical vibrations should be infrared inactive. There is also no theory at present predicting that combination modes should be active. On the other hand, our experiments indicate that the absorption is not sensitive to lattice imperfections, either those arising from chemical impurities or those arising from the disorder produced

TABLE I. Constants and calculated values of the ratio in Eq. (1) for germanium, silicon, and diamond.

		Germanium	Silicon	Diamond	
c_{11}	10^{12} dynes/cm^2	1.29	1.67	9.5	
c_{12}	10^{12} dynes/cm^2	0.48	0.65	3.9	
c_{44}	10^{12} dynes/cm^2	0.67	0.80	4.3	
m	10^{-23} gram	12.05	4.658	1.995	
a	A	5.65	5.42	3.56	
ν_1	cm^{-1}	340	610	2175	($\nu_0=1332$ cm^{-1})
Ratio (1)		1.06	1.12	1.05	1.40

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[15] Y. S. Hsieh, Phys. Rev. **85**, 730 (1952).

by nucleon bombardment. Moreover, an absorption due to lattice imperfection may become sharper at low temperature but would not be expected to show an over-all decrease as found experimentally. The observed temperature dependence seems to indicate that the absorption is made possible by the thermal vibrations of the atoms. One might assume that the dipole moment induced by a vibrational mode is in the first approximation proportional to the root-mean-square thermal displacement $(\langle r^2\rangle_{Av})^{\frac{1}{2}}$. The absorption should then be proportional to $\langle r^2\rangle_{Av}$. Lonsdale[16] has shown that

$$\langle r^2\rangle_{Av}=\frac{4.364\times10^{-14}}{A\theta}\left\{\frac{\phi(\beta)}{\beta}+\frac{1}{4}\right\}, \tag{2}$$

where θ is the Debye temperature, A is the atomic weight,

$$\beta=\theta/T,$$
$$\phi=\frac{1}{\beta}\int_0^\beta\frac{\xi d\xi}{e^\xi-1}. \tag{3}$$

Figure 5 gives the calculated curves for germanium, silicon, and diamond. The values of θ used are 363°K, 658°K, and 2340°K[16] for the three substances, respectively. The curves are plotted with $\langle r^2\rangle_{Av}$ for 5°K normalized to unity. The relative magnitudes of the strongest absorption peak measured at different temperatures for germanium and silicon are given by the circles and crosses, respectively. The good fit between the points and corresponding curves confirms the proportionality between the absorption and $\langle r^2\rangle_{Av}$. The 5°K points show some deviation, being low for silicon and somewhat high for germanium. However, as explained above, the accuracy of the measurements for this temperature was not as good as for the higher-temperature measurements.

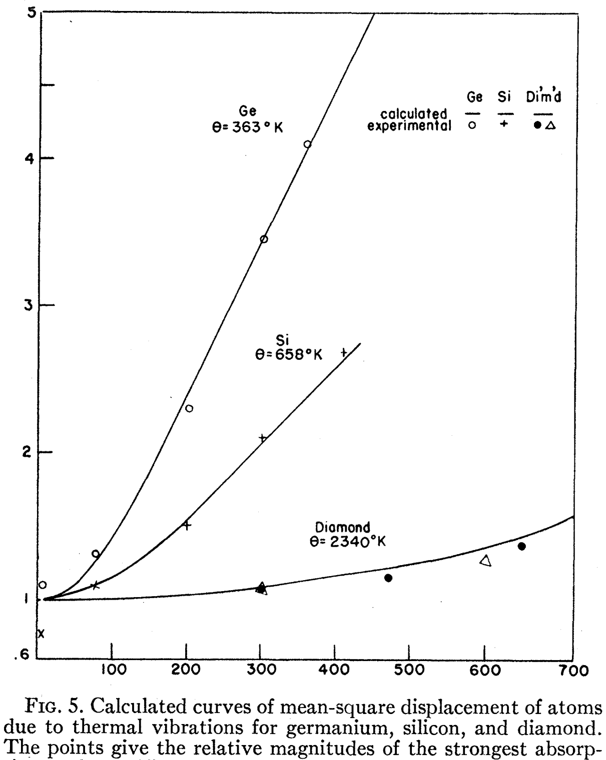

Fig. 5. Calculated curves of mean-square displacement of atoms due to thermal vibrations for germanium, silicon, and diamond. The points give the relative magnitudes of the strongest absorption peak at different temperatures. The 2175-cm^{-1} peak is used for diamond.

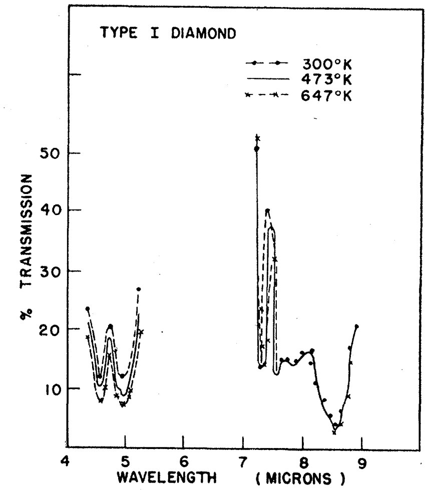

Fig. 6. Transmission curves for a type I diamond specimen at different temperatures.

In the case of diamond Robertson, Fox, and Martin[6] found no significant variation of absorption in the temperature range 80°K to 300°K. The curve for diamond in Fig. 5 shows that we should expect the change of absorption in this temperature range to be small as a result of the high Debye temperature. Consequently measurements were made at higher temperatures on two specimens of type I diamond. Figure 6 gives the transmission curves showing the prominent absorption peaks for one of the samples. It is known that the group of absorption bands at shorter wavelengths is present in all diamonds and is the only one present in type II, whereas the group of bands at longer wavelengths varies from specimen to specimen. It is seen that the short-wavelength group varied with temperature while the long-wavelength group was temperature-insensitive. The second specimen showed the same behavior. The triangles in Fig. 5 gives the relative absorption at different temperatures for the 2175-cm^{-1} band in the short-wavelength group taken on one specimen and the filled circles gives the data taken on the other specimen. The points are seen to be in fair agreement with the calculated curve.

The results of these measurements lead to the following conclusions:

(A) The absorption observed in germanium and silicon is similar in nature to the absorption in type II diamond.

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(B) This absorption seems to be proportional to the mean-square thermal displacement of the atoms, indicating that it is made possible by the disturbance of the lattice symmetry.

(C) The frequency of the strongest peak in germanium and silicon satisfies the relation (1) fairly well. The frequency of the strong band in type II diamond, 2175 cm^{-1}, is also in good agreement with this relation (see Table I). However, the Raman shift in diamond gives a quite different value for ν_0, 1332 cm^{-1}, which does not satisfy (1). It would seem that rather than arising from errors in the values of the elastic constants, the discrepancy is due to the inaccuracy of relation (1) for reasons pointed out by Born.

(D) The long-wavelength absorption bands in diamond, which varies from specimen to specimen and is temperature-insensitive, seems to be due to lattice imperfections, e.g., impurities.

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Nuclear Alignment at Low Temperatures

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The population distribution of nuclei aligned at low temperatures is derived by means of an expansion of the density matrix in powers of A/kT with an arbitrary external field. It is shown how this is related to the angular distribution of emitted γ radiation. The influence of interionic exchange and dipole coupling is examined to order $(A/kT)^3$ and is found to be generally small and cannot account for some experimental results. The case of finite crystal field interaction is considered as it applies to the angular distribution.

I. INTRODUCTION

FOR the interpretation of early experiments on nuclear alignment at low temperatures it was found sufficient to assume a rather simple picture of the process.[1,2] However, recent experiments at Oxford[3] have made further study of the problem necessary. It will be recalled that radioactive isotopes are substituted in a salt whose low-temperature properties are known and nuclear alignment is detected through the anisotropic distribution of the emitted γ radiation.

The early experiments[4] depended on the anisotropic hfs shown by some salts in their microwave absorption spectra. Among the assumptions made in the theory of this effect were: (a) that the crystalline field splitting of the ionic states was large enough that at low temperatures only the ground state doublet was occupied and the ion could be described by a fictitious "ionic spin," $S=\frac{1}{2}$, and anisotropic g values; (b) that interionic forces between neighboring ions could be ignored insofar as nuclear alignment was concerned.

The recent series of experiments[3] were done on a Ce–Co salt containing Co^{60}. These depended on the above effect and also on the application of an external magnetic field to polarize part of the ions which then in turn through the (nearly isotropic) hfs coupling polarized their nuclei. Theoretical curves were drawn, for various values of field, of the variation with temperature of the anisotropy ϵ in the emitted radiation.[5] If $F(\beta)$ is the angular distribution, ϵ is defined as $\epsilon=[F(\frac{1}{2}\pi)-F(0)]/F(\frac{1}{2}\pi)$. On comparing these with the experimental data, good agreement was found for strong fields, but in zero field the anisotropy was much less ($\sim$5 percent) than that calculated ($\sim$25 percent). This disagreement was tentatively attributed to dipole coupling between the Ce and Co ions. This influence would be expected to diminish in strong external fields. Dipole coupling between the Ce ions is known to account for the susceptibility of this salt.[6]

A further series of experiments are planned in which the first assumption, i.e., that of large crystal field splitting, will not hold.

The purpose of this paper is to examine the influence of interionic (exchange and dipole) forces on the degree of nuclear alignment and to include the case where the crystal field splitting is only of the same order as other forces.

II. GENERAL

In previous work[1] nuclear alignment was discussed in terms of the relative populations, or probabilities of the $2I+1$ magnetic substates of the nucleus. Let W_M be the probability of the state with z component of spin M ($\hbar$ units) and $F_M(\beta)$ be the angular distribution of radiation from that state, then the total angular distribution is $F(\beta)=\Sigma_M W_M F_M(\beta)$.

To obtain W_M, a general approach is to consider the

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* National Research Laboratories Postdoctorate Fellow.

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