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Nitrogen, A Major Impurity in Common Type I Diamond

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Common type I diamonds (as classified by Robertson *et al.*) have additional absorption in the infrared and ultraviolet. It is shown that the strongest absorption band in the infrared at 7.8 μ and the ultraviolet absorption at 3065 A are proportional to the nitrogen concentration of the crystal. A corresponding increase in lattice constant is found to be as high as 0.01% for a nitrogen content of 0.2%. Concentration, X-ray, and density data suggest that nitrogen occupies a substitutional position in the diamond lattice. The infrared absorption bands at 7.8, 8.3, 9.1, and 20.8 μ are considered to be C-N molecular vibrations. Several optical, electrical, and thermal properties of diamond are discussed in view of our findings.

INTRODUCTION

TWENTY-FIVE years ago Robertson, Fox, and Martin[1] reported striking differences in the optical and photoconductive properties of diamonds. They classified diamonds into Type I and Type II according to their differences in the ultraviolet and infrared transmission. The rarer type II crystals exhibit absorption bands between 3 and 6 μ only and a sharp absorption edge in the ultraviolet below 2250 A. The more common (approximately 95%) specimens of Type I show additional absorption bands between 6 and 13 μ and a tail on the absorption edge both of which vary considerably from specimen to specimen.[2,3] With increasing absorption between 6 and 13 μ, the absorption in the ultraviolet increases, shifting the tail of the absorption edge to approximately 3000 A.[1,3,4]

Recent experimental and theoretical work has given strong evidence that the absorption bands between 3 and 6 μ are lattice bands of the diamond lattice proper.[5–8] These absorption bands are found to be of the same intensity in all diamonds[4–9] and the absorption increases uniformly with increasing temperature similarly to the lattice bands in silicon and germanium.[5]

There has been a considerable amount of speculation as to the origin of the additional absorption in diamonds of Type I. Frequently, impurities were considered to be the cause. Extensive experimental work using spectrographic[10] and neutron activation techniques[11] revealed indeed considerable concentrations of impurities. Aluminum, calcium, silicon, and several other elements were found in diamonds of gem quality in concentrations as large as 10^{18} impurity atoms per cm^3. However, these impurities were found in both types of diamonds in similar concentrations. They could not be related to the optical or electrical properties characteristic of Type I diamonds.

Several authors suggested that carbon atoms in interstitial lattice positions or carbon vacancies[6] or clusters of vacancies or cavities[12] in the diamond structure were responsible for the existence of Type I diamonds. As a test for this hypothesis diamonds were bombarded with fast electrons, neutrons, deuterons, and γ rays.[6,13,14] Measurements gave evidence for the formation of interstitial carbon atoms and carbon vacancies.[14] Infrared absorption between 6 and 13 μ, however, could not be produced in any of these bombardment experiments.

Raman[15] proposed a new theory of the diamond lattice and suggested the existence of two types of diamond lattices in order to solve the Type I problem in diamond. His theory of lattice dynamics, however, is not generally accepted.[4,16]

Investigations on high-purity (electrically active impurity concentration $<10^{14}$ cm^{-3}) silicon[17,18] and germanium[19] showed that these crystals can contain considerable amounts of dissolved gases. In particular oxygen in silicon has received considerable attention. Concentrations up to 2×10^{18} oxygen atoms per cm^3 were found in silicon single crystals.[17] Infrared absorption bands corresponding to silicon-oxygen molecular

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[10] F. G. Chesley, Am. Mineralogist **27**, 20 (1942); M. E. Straumanis and E. Z. Aka, J. Am. Chem. Soc. **73**, 5643 (1951); F. A. Raal, Am. Mineralogist **42**, 354 (1957), and Proc. Phys. Soc. (London) **71**, 846 (1958); E. N. Bunting and A. Van Valkenburg, Am. Mineralogist **43**, 102 (1958).

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[14] Griffiths, Owen, and Ward; M. C. M. O'Brien and M. H. L. Pryce; Ditchburn, Mitchell, Paige, Custer, Dyer, and Clark. *Proceedings of the Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955).

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vibrations were observed[20] and quantitatively related to the oxygen content of the specimen.[17]

We have investigated the gas content of diamond crystals. As a result of this investigation we found large nitrogen concentrations in diamonds of Type I. We are able to show that the nitrogen content can be quantitatively correlated with the infrared absorption around 8 μ, the ultraviolet absorption below 4000 A, and with the expansion of the diamond lattice. These observations are strong evidence that nitrogen as an impurity is the major cause for the properties characteristic for Type I diamonds.

EXPERIMENTAL

All the diamonds investigated were of gem quality, free of flaws or inclusions. Several crystals showed a slight yellow color due to absorption in the near ultraviolet.[13] Most specimens were completely colorless.

Infrared measurements were made on polished crystals with thicknesses between 0.4 mm and 3 mm. A Perkin Elmer double-beam instrument was used to obtain a general picture of the absorption spectrum of the specimens. Quantitative measurements at significant wavelengths were made with a Perkin Elmer double-pass spectrometer. Ultraviolet data were obtained using a Cary recording spectrophotometer. The absorption coefficients were calculated taking multiple reflections into account with $n=2.39$ between 6 and 13 μ and $n=2.50$ in the ultraviolet.[21,22]

The gas content of diamond crystals was determined in a system which is normally used for vacuum fusion gas analysis. The specimen was heated to 2000°C in a carbon crucible and the gas content freed during the graphitization of the crystal was analyzed for CO, H_2, and residual gases. In several cases the gas evolved was investigated by means of a mass spectrometer. The residual gas was found to be nitrogen, N^{14}.

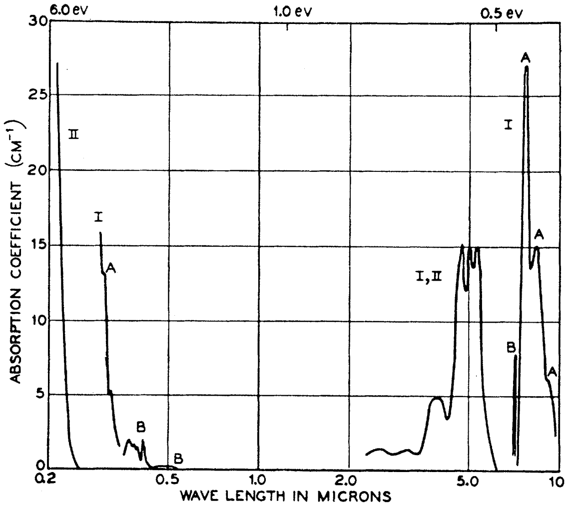

FIG. 1. Absorption spectra of Type I and Type II diamonds.

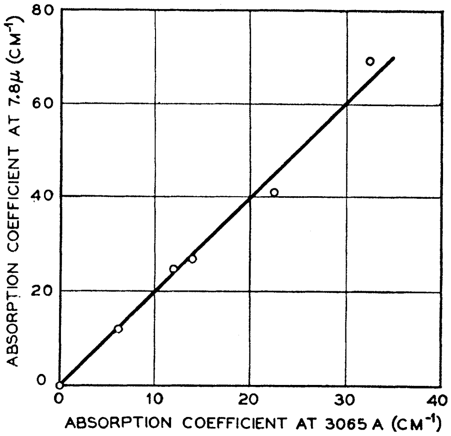

FIG. 2. Absorption at 3065 A *versus* absorption at 7.8 μ for several diamonds.

The lattice constant of diamonds was measured with a high-precision crystal spectrometer. On this instrument high orders of reflections on both sides of zero were measured by using a very fine beam and a circle which reads to one second. Eccentricity, absorption, and radius errors are eliminated by this design. We used copper $K\alpha$ radiation on the (331) plane, taking a mean of four determinations made on different parts of the divided circle. The temperature was carefully controlled. The instrument will be described in a forthcoming paper.[23]

The difference in density between diamond crystals of varying nitrogen content was investigated in a system similar to that of Bearden.[24] A glass tube containing a solution of thallous formate in water and two diamond crystals were placed into a thermostated bath the temperature of which could be measured to better than 10^{-2}°C. The density difference of the two crystals under consideration could be determined as follows:

a. The temperature of the thermostat was adjusted in such a way that the two crystals just floated. After a small increase in the temperature of the bath, the crystal with the higher density starts to sink. The temperature difference necessary to make the second crystal sink is a measure of the density difference of the two crystals. The change in density of our solution as a function of temperature was determined separately.

b. When both crystals sink simultaneously, their density difference can be estimated from the speed of sinking, the viscosity of the solution, and the crystal dimensions.

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RESULTS

The optical spectrum between the ultraviolet absorption edge and $10\,\mu$ of a Type I and a Type II diamond is presented in Fig. 1. As pointed out above, both crystals have the same absorption bands between 2 and $6\,\mu$ but different absorption between 6 and $10\,\mu$ and in the ultraviolet.

Sutherland *et al.*[6] subdivided the additional infrared absorption into group *A* with broad absorption bands at 7.8, 8.3, 9.1, and $20.8\,\mu$, and group *B* with sharper and generally smaller band at 7.0, 7.3, 7.5, 8.5, 10.0, 12.9, and $30.5\,\mu$ (only the strongest at $7.3\,\mu$ is shown in Fig. 1). The intensity of the group *B* bands is related to the strength of a group of absorption peaks following a main band at 4155 A. With increasing absorption of the group *A* bands, the ultraviolet absorption shifts to longer wavelengths.[6] At room temperature two bands at 3060 and at 3155 A can be seen in Fig. 1. We measured the infrared and ultraviolet absorption of several diamond crystals in order to find a quantitative relation between these two properties. In Fig. 2 the absorption coefficient of the band maximum at $7.8\,\mu$ is plotted as a function of the absorption at 3060 A of the same specimen. There is good proportionality between the group *A* absorption in the infrared and the ultraviolet. The absorption coefficient at $7.8\,\mu$ is twice the absorption coefficient at 3060 A.

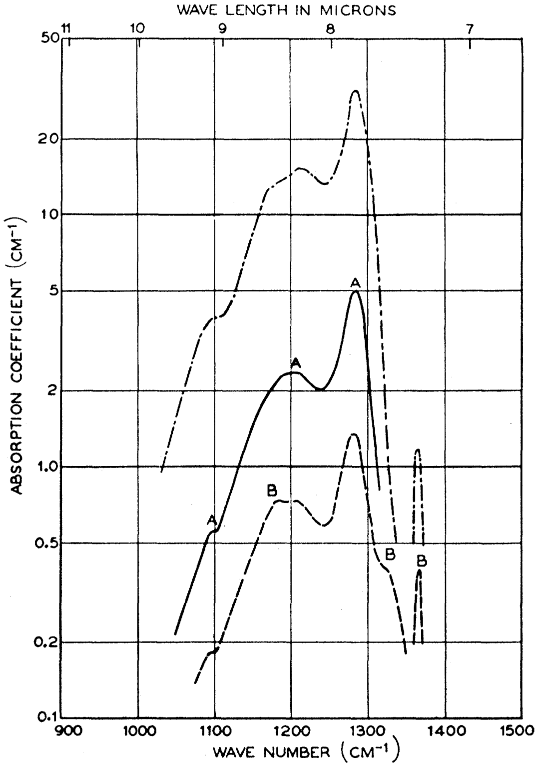

FIG. 3. Absorption spectra for 3 diamonds showing constant form of *A* bands.

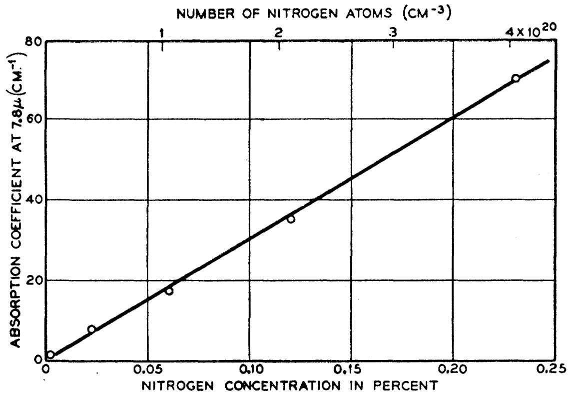

FIG. 4. Nitrogen content *versus* absorption coefficient at $7.8\,\mu$.

Figure 3 gives the absorption of three different diamond crystals between 7 and $10\,\mu$. It appears from the semilog plot that the total absorption spectrum of the group *A* bands has the same form in all crystals after the small additions of group *B* bands are subtracted. The maximum of the strongest absorption band is located at $7.8\,\mu$. The group *A* absorption bands change very little with temperature. We found that the three group *A* bands at 7.8, 8.3, and $9.1\,\mu$ shifted to shorter wavelength by only $10^{-2}\,\mu$ ($\sim 2\times 10^{-4}$ ev) between 300°K and 5°K. The intensity of this absorption was found to be independent of temperature.

Several diamond crystals were analyzed for their gas content. Large concentrations of nitrogen were found besides small quantities of CO and H_2. In Fig. 4 the absorption coefficient of the band maximum at $7.8\,\mu$ is plotted as a function of the nitrogen concentration of the same crystals. The empirical straight line connecting the experimental points goes through the origin indicating that the whole absorption of the group *A* bands is proportional to the nitrogen concentration in the specimen. It should be pointed out that the nitrogen concentration of 4×10^{20} nitrogen atoms per cm^3 found in the crystal with an absorption coefficient of $\alpha(7.8\,\mu) = 70$ cm^{-1} is equivalent to the density of nitrogen atoms in a gas at seven atmospheres of pressure.

In order to find out where the nitrogen is located in the diamond lattice, the changes in lattice constant and density were determined for a number of diamond crystals. In Fig. 5 the absorption coefficient at $7.8\,\mu$ is plotted as a function of the lattice constant at room temperature. Figure 5 (together with Fig. 4) shows a distinct increase in lattice constant with increasing nitrogen content. A Type II crystal (no absorption between 6 and $13\,\mu$, ultraviolet absorption edge at 2250 A) had the smallest lattice constant of $3.56683 \pm 1\times 10^{-5}$ A while the most highly Type I crystal with $\alpha(7.8\,\mu) = 70$ cm^{-1} exhibited the largest lattice

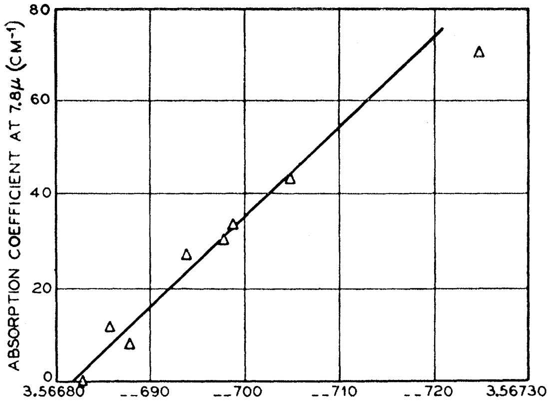

FIG. 5. Lattice constant *versus* absorption coefficient at 7.8 μ.

constant[25] of $3.56725 \pm 3\times10^{-5}$ A. Thus the relative change in lattice constant can be as high as 10^{-4}. If nitrogen is substituted for a carbon atom in a normal lattice site, the relative change in density $\Delta\rho/\rho$ is expected to be

$$\frac{\Delta\rho}{\rho}=c\left(\frac{M_N-M_c}{M_c}\right)-3\left(\frac{\Delta a}{a}\right),$$

where M_N and M_c are the atomic masses of nitrogen and carbon, c is the nitrogen concentration and $\Delta a/a$ the relative change in lattice constant. Since M_N and M_c are 14 and 12, respectively, we obtain, for $c=0.1\%$ and a corresponding $\Delta a/a=5\times10^{-5}$,

$$\Delta\rho/\rho=1.67\times10^{-4}-1.5\times10^{-4}\cong10^{-5},$$

i.e., the increase in weight is very nearly compensated by an increase in lattice constant. On the other hand on the assumption of nitrogen in an interstitial position

$$\begin{aligned}\Delta\rho/\rho&=c(M_N/M_C)-3(\Delta a/a)\\&=11.6\times10^{-4}-1.5\times10^{-4}\cong10^{-3},\end{aligned}$$

i.e., the expected density change in two orders of magnitude larger. Our density measurements did not show any change in density between a diamond of Type II and crystals with nitrogen concentrations up to 4×10^{20} atoms per cm^3. Our experimental accuracy for $\Delta\rho/\rho$ was better than 10^{-5}. This result may be taken as experimental proof that nitrogen occupies a substitutional position in the diamond lattice.

DISCUSSION

Since the time of Robertson's article,[1] extensive research has shown that a number of important physical properties of diamond vary considerably depending upon the type of diamond under investigation. Several of these properties will be discussed now in view of our findings.

Ultraviolet Absorption

The band structure of diamond has received considerable theoretical attention. The most recent calculations by Herman[26] suggested an energy gap E_G of approximately 6 ev. The sharp rise in the ultraviolet absorption of Type II diamonds at 2250 A (5.6 ev) can be considered as the true absorption edge of the pure diamond lattice. In diamond of Type I absorption extends to considerably longer wavelength.[1] The shift in absorption to longer wavelengths and the corresponding increase of the absorption of 3065 A is proportional to the intensity of the group A bands, i.e., to the nitrogen concentration (see Fig. 2 and 4). Using thin cleaved diamond specimens, Custers[27] has shown that the additional absorption of Type I diamonds merges into the main absorption edge for absorption coefficients of several hundred cm^{-1}. The absorption of Type I diamonds for $\lambda > 2250$ A has therefore to be considered as a tail on the true absorption edge of diamond. Two causes might be cited for the absorption in the ultraviolet.

a. The lattice expansion of diamond with increasing nitrogen content indicates considerable changes of the normal diamond lattice in the neighborhood of the nitrogen impurity. Local deformation of the crystal lattice gives rise to a deformation of the electronic band structure in this region which can result in a decrease in the separation between conduction and valence band.[28] As a result electronic transitions and a corresponding absorption for photons having energies for $h\nu < E_G$ will be expected.

b. Nitrogen in a substitutional lattice site will give rise to energy levels within the forbidden zone. Diamond shows no absorption in the visible or infrared which could be related to electronic transitions to these energy levels. This fact indicates that nitrogen forms deep-lying energy levels in diamond. (Note that diamond is an insulator with approximately 10^{15} ohm cm at 300°K). The absorption band at 3155 A (3.9 ev), however, which is superimposed on the absorption tail and which increases with increasing absorption at 7.8 μ (i.e., with increasing nitrogen concentration) might correspond to transitions from the conduction band to these deep lying donor states. Robertson found indeed in Type I diamonds enhanced photoresponse around 3200 A which would be expected from the photoionization of these impurity levels.

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[25] The lattice constant of this crystal could be determined to $\pm3\times10^{-5}$ A only, because of a broadened x-ray reflection peak. The accuracy for most crystals was $\pm1\times10^{-5}$ A.

[26] F. Herman, Phys. Rev. **93**, 1214 (1954).

[27] J. F. H. Custers and F. A. Raal, Nature **179**, 268 (1957).

[28] The change in energy gap δE_G is given by: $\delta E_G = |E_{1G}|\delta V/V$. For diamond E_{1G} is of the order of 10 ev and $\delta V/V$ is approximately 10%. Therefore δE_G is estimated to be 1 ev. [For a discussion of the deformation potentials see W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, New York, 1950)].

Infrared Absorption

The absorption bands between 2 and 6 μ are true lattice bands as discussed above. They are independent of the nitrogen concentration of the crystal. A possible explanation for the infrared absorption resulting from the nitrogen content in diamond is as follows: If nitrogen is substitutionally bound to carbon atoms, then C-N molecular vibrations are expected. In a simplified picture one might assume the nitrogen atom to be located in the center of a tetrahedron of carbon atoms. The corresponding symmetry of point group T_d predicts two (triply degenerate) infrared active vibrations. The observed absorption bands at 7.8 μ and 20.8 μ might be assigned to the C-N stretching (ν_3) and bending (ν_4) vibration, respectively.[29] This picture needs some refinement. Nitrogen [electronic state of the atom $(1s)^2\,(2s)^2\,(2p)^3$] is tetrahedrally bound in the diamond lattice by four sp^3 orbitals. Such a valence state of nitrogen requires that one nitrogen electron be promoted to the $3s$ orbital. In the electrostatic field created by the four sp^3 bonds this $3s$ electron will be strongly polarized to minimize the Coulomb energy of the system. Symmetry arguments suggest that a minimum energy will be obtained when ths extra electron is more strongly concentrated around one of the four C-N bonds. This fact is evidenced by the deep-lying impurity levels discussed above and is substantiated by paramagnetic resonance experiments.[30] The Coulomb repulsion resulting from this additional electron will serve to expand the C-N distances, with a particularly strong expansion of this C-N bond around which the $3s$ electron is concentrated. As a result the lattice constant of diamond increases when nitrogen is present in the lattice (see Fig. 5). The distorted tetrahedron around each nitrogen impurity belongs to the point group C_{3v}, where six infrared active vibrations are expected.[31] The three absorption bands at 7.8, 8.3, and 9.1 μ are considered to be the three C-N stretching vibrations, while the absorption band at 20.8 μ is the only bending vibration observed so far.[32]

It is interesting to note that cyclic polyamines show a strong absorption band around 9 μ which has been attributed to a C-N stretching vibration. An absorption cross section of 10^5 cm^2/mole was reported[33] which would predict an absorption coefficient of 66 cm^{-1} for a nitrogen concentration of 4×10^{20} nitrogen atoms per cm^3. The agreement with our measured absorption coefficient of 70 cm^{-1} is unexpectedly good. It indicates that molecular vibrations can account for the infrared absorption in diamond I.

At present we cannot rule out the possibility that the infrared absorption corresponds to an otherwise forbidden lattice vibration of the diamond lattice[6,7] which is induced by the presence of nitrogen as an impurity. It is worth pointing out that plastic deformation, bombardment with high-energy nucleons (producing 10^{19} lattice defects per cm^3), and doping with approximately 10^{18} impurity atoms per cm^2 did not alter the lattice absorption in germanium.[5]

Birefringence

Because of the cubic symmetry of the diamond lattice, diamond crystals are expected to be optically isotropic. However, Robertson *et al.*[1] showed that Type I diamonds exhibit patterns of birefringence when viewed between crossed nicols. In fact, all our crystals with absorption bands between 6 and 10 μ are birefringent. This observation can be explained as follows. It was shown above that the diamond lattice expands with increasing nitrogen concentration. Local fluctuations in the nitrogen content will introduce strain into the crystal and give rise to a birefringence pattern. One diamond which showed distinct birefringence lines was examined more quantitatively (with a Berek compensator). The difference in index of refraction, of two perpendicularly, polarized rays was found to be $\Delta n=1.9\times10^{-6}$.

Diamond is known to be isotropic in its stress-birefringence behavior.[34] The stress birefringence constant is $q=3\times10^{-14}$ cm^2/dyne. Hence we can calculate the stress in the bright lamination[35]:

$$T=2\Delta n/qn^3=1.4\times10^8 \text{ dynes/cm}^2.$$

Knowing the elastic constants of diamond, $c_{11}=10.8\times10^{12}$ dynes/cm^2 and $c_{12}=1.25\times10^{12}$ dynes/cm^2,[36] the corresponding strain $\Delta a/a$ is determined from elastic theory[37] to be

$$\frac{\Delta a}{a}=\frac{c_{11}T}{(c_{11}-c_{12})(c_{11}-2c_{12})}=1.2\times10^{-5}.$$

From Fig. 4 and Fig. 5 it can be inferred that a difference of $\Delta c=4\times10^{19}$ nitrogen atoms per cm^3 in various parts of the crystal will change the lattice constant by $\Delta a/a=1.2\times10^{-5}$. Therefore, fluctuation of the nitrogen

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[29] For a valence force model reasonable values were calculated for k, the bond-stretching, and for $k\delta/l^2$, the bending force constant: $k=4.8\times10^5$ dynes/cm and $k\delta/l^2=0.46\times10^5$ dynes/cm. See reference 31.

[30] Smith, Gelles, and Sorokin, Bull. Am. Phys. Soc. Ser. II, 4, 144 (1959).

[31] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, New York, 1945).

[32] In going from the T_d symmetry to C_{3v} the degeneracies are partly removed; each of the triply degenerate vibrations ν_3 and ν_4 splits into a nondegenerate and a double-degenerate vibration. The two vibrations ν_1 (pulsing) and ν_2 (deformation), which are only Raman active in T_d, become infrared active in the C_{3v} point group.

[33] Dietrich, Zahn, and Spoor, Z. Naturforsch. **12b**, 665 (1957). An infrared absorption band 7.9 μ, corresponding to a C-N vibration has been observed in $N(CH_3)_3$. S. H. Bauer and M. Blander, J. Molecular Spectroscopy (to be published).

[34] E. Poindexter, Am. Mineralogist **40**, 1032 (1955).

[35] W. Bond, Bell System Tech. J. **22**, 1 (1943). Equation (18.1) can be rewritten: $q\times T=1/n_a{}^2-1/n_b{}^2\sim2\Delta n/n^3$; n_a and n_b are the refractive indices as altered by the applied stress.

[36] H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957).

[37] C. Kittel, *Solid-State Physics* (John Wiley & Sons, Inc., New York, 1953); and reference 35.

concentration in neighboring regions of the crystal can account for the observed birefringence effects.[38] Obviously varying amounts of nitrogen are incorporated into diamond crystals during the growth process. In this connection it should be mentioned that birefringence has been observed in silicon crystals which were pulled from a melt (which was contained in a quartz crucible[17]). Birefringence patterns were found corresponding to fluctuations of $\Delta c \sim 10^{17}$ oxygen atoms per cm^3 in the crystal.[39]

Photoconductivity and Crystal Counting

It has been known for many years that diamond is photoconductive when irradiated with ultraviolet light.[1,3,5,40] The photoconductive response (photocurrent per incident energy *versus* wavelength) was found to be smaller in Type I diamonds.[1] Extensive investigations are reported on the application of diamonds as crystal counters.[41] It was shown that the counting efficiency varies strongly from diamond to diamond and in some cases strong fluctuations were observed even within the same specimen.[42] The counting efficiency decreases with increasing ultraviolet absorption below 3000 A.[42] From Ahearn's data and from infrared measurements on the same crystal, one can estimate that the counting efficiency decreases by two orders of magnitude in that part of the crystal where the nitrogen content increases to approximately 10^{20} nitrogen atoms per cm^3 in the crystal. All the present information seems to indicate that nitrogen as an impurity has a deteriorating effect on the photoconductivity and counting efficiency of diamond crystals. This is not surprising since the large impurity concentration found will not only reduce lifetime[43] and charge carrier mobility,[44] but also may produce variations in the trap density. More quantitative experimental data correlating the electrical and optical properties of diamond crystals are urgently needed.

Thermal Conductivity

The theory of conductivity of dielectrics predicts a strong maximum of thermal conductivity at low temperature.[45,46] Such a maximum has been observed for a number of dielectrics.[47] Diamond crystals of Type I, however, show an unexpectedly low (29 w/cm deg) thermal conductivity, which is nearly constant between 20 and 120°K.[48] It was pointed out by Pomeranchuck that scattering of phonons at point imperfections can account for the observed temperature conductivity.[45] In fact, Pomeranchuck estimated a defect concentration of 4×10^{-4} from the experimental data.[45] It was shown above that nitrogen in concentrations up to 2×10^{-3} was found in diamond crystals. Therefore nitrogen has to be considered as a possible cause for the abnormal thermal conductivity in Type I diamonds. It is of great interest in this respect that Berman *et al.* reported more recently on measurements on Type IIa crystals.[49] They found indeed a pronounced maximum of thermal conductivity (~150 w/cm deg) at 80°K.

FINAL REMARKS

In this article we have concentrated on the relation between the nitrogen concentration and the group *A* absorption in Type I diamond. Most of our crystals had relatively small absorption corresponding to group *B* bands. At present there is no indication that nitrogen is connected with the group *B* absorption in diamond. The possibility that oxygen (or hydrogen) is involved in the group *B* absorption has to be substantiated by more experimental work.

There are several properties of diamond which were reported to depend upon the type of diamond under investigation. Extra streaks in the Laue pattern (secondary extra reflections)[50], 222 reflections,[51] fluo-

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[38] Optical measurements on the (inhomogeneous) crystal discussed here indicate an average nitrogen concentration of approximately 2×10^{20} nitrogen atoms per cm^3. In this specimen the birefringence pattern was particularly strong. Birefringence caused by Δc of the order of 10^{18} nitrogen atoms per cm^3 should be detectable in diamond crystals.

[39] W. C. Dash, *Proceedings of the International Conference on Crystal Growth and Perfection of Crystals* (John Wiley & Sons, Inc., New York, 1958), p. 383.

[40] B. Gudden and R. Pohl, Z. Physik **16**, 170 (1923); A. G. Redfield, Phys. Rev. **94**, 526 (1954).

[41] Wooldridge, Ahearn, and Burton, Phys. Rev. **71**, 913 (1947); K. G. McKay, Phys. Rev. **74**, 1606 (1948); and **77**, 816 (1950). A. G. Chynoweth, Phys. Rev. **83**, 254 and 264 (1951); G. P. Freeman and H. A. van der Velde, Physica **16**, 486 (1950); **17**, 565 (1951).

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[44] Hole mobilities of 1500 cm^2/v sec were found in semiconducting diamonds (IIb) [J. F. H. Custers, Physica **18**, 489 (1954); and **20**, 183 (1955); Nature **176**, 173 (1955); W. J. Leivo and R. Smoluchowski, Phys. Rev. **98**, 1532 (1955); I. G. Austin and R. Wolfe Proc. Phys. Soc. **B69**, 329 (1956)]. Similar mobility values were estimated from photoconductivity and crystal counting studies.

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[46] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

[47] R. Berman, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1953), Vol. 2, p. 103; Carruthers, Geballe, Rosenberg, and Ziman, Proc. Roy. Soc. (London) **A238**, 502 (1957); T. H. Geballe and G. Hull, Phys. Rev. **110**, 773 (1958).

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rescence,[4,52] and polarized luminescence[53] were observed in Type I diamonds but data concerning the intensity of the ultraviolet or infrared absorption of the same specimen are usually lacking. More quantitative measurements are necessary before possible connections between the effects mentioned and the nitrogen concentration of the crystal can be established. The data reported here should facilitate such investigations.

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Nonresonant Nuclear Spin Absorption in Lithium, Sodium, and Aluminum

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Audio-frequency spin absorption has been observed in the nuclear spin systems of the metals lithium, sodium, and aluminum. In lithium and sodium, the observed second moment of the absorption line at zero dc magnetic field is in agreement with calculations assuming only magnetic dipole-dipole interactions; in aluminum the zero-field absorption extends to frequencies as high as 50 kc/sec and the second moment of the absorption line appears to be about 50% larger than expected. Spin absorption has also been observed at small applied dc magnetic fields, H_0, for audio-frequency magnetic excitation both parallel to and perpendicular to H_0. In both of these cases, absorption occurs at γH_0 and $2\gamma H_0$ in agreement with theory.

INTRODUCTION

THE well-known phenomenon of nuclear magnetic resonance in nuclear spin systems in solids is characterized by the use of applied dc magnetic fields which are large in comparison with the internal dipole-dipole fields and by absorption of energy from an rf magnetic field at the Larmor frequency. This absorption has a line width determined by the internal fields, if one neglects relaxation effects, and characterized by $\langle(\Delta H)^2\rangle_{\mathrm{Av}}$, the second moment of the line in gauss^2. As Van Vleck[1] has shown, $\langle(\Delta H)^2\rangle_{\mathrm{Av}}$ can be calculated from basic principles.

At dc magnetic fields which are not large in comparison with the internal fields, the nature of the absorption spectrum changes significantly. In particular, at zero dc field the absorption spectrum is determined solely by the spin-spin interactions, assuming that electric quadrupole interactions with the lattice are negligible. In this case the spectrum extends from zero frequency to frequencies of order $(\gamma^2\langle(\Delta H)^2\rangle_{\mathrm{Av}})^{\frac{1}{2}}$, where γ is the nuclear gyromagnetic ratio. At dc magnetic fields, H_0, which are comparable with the internal fields, the spectrum is composed of several parts. First, it is characterized by absorption with the applied ac magnetic field, H_1, either parallel to or perpendicular to the dc field. Second, the spectrum is composed of several lines; the dipole-dipole interaction contains matrix elements which allow transitions and absorption of energy around zero frequency, at γH_0, at $2\gamma H_0$, and at higher frequencies. The intensity of absorption in the parallel case, and of the absorption at frequencies other than γH_0 in the perpendicular case, decreases as a power of $\langle(\Delta H)^2\rangle_{\mathrm{Av}}/H_0^2$. At high field all lines except the Larmor line are of low intensity and one has the usual magnetic resonance case.

The theory of spin absorption at small dc fields has been treated by Broer[2] and Wright.[3] These authors calculate properties of the spin system by the diagonal sum method and, although the problem cannot be solved exactly, are able to derive the nth moments of the zero-field line and the variation of the lines with field. Experimental results in electron paramagnetic systems, obtained by Gorter[4] and co-workers and others, have been compared with the theory with limited agreement. In the systems reported, spin absorption at zero field extends from zero to hundreds of megacycles and the experimental investigations have usually been limited to the low-frequency part of the line. Nuclear

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