The Effect of Inhomogeneities on the Electrical Properties of Diamond

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To account for the non-uniformities in the electrical properties of diamond, particularly those observed in bombardment conduction, the proposal is made that the well-known lattice imperfections are not distributed homogeneously in the physical crystal, and that the resulting fluctuations in the height of the energy bands relative to the Fermi level might produce interspersed "pools of mobile charge" separated by barriers within the diamond. These pools and barriers should lead to dielectric losses at high frequencies. A single conducting channel, in series with a barrier, could be represented by a series resistance R_s and capacity C_s or by the equivalent parallel resistance R_p and capacity C_p.

With some, but not all, diamonds measurable dielectric losses at 70 mc/sec were observed. R_p varied from 5×10^6 ohms, the limit of measurement, to 4×10^5 ohms. Furthermore, the proposed model suggests that, in some cases, these barriers might be sufficiently lowered to establish a dc conducting channel all the way through a crystal. With a few of the lossy diamonds precisely this phenomenon of "high conduction" has been observed, in which a resistance of the order of a megohm is obtained with a dc voltage applied. This current appears abruptly in time but it lags behind the application of the voltage. This lag is influenced by irradiation with light or alpha-particles or by previous treatment.

The proposed pools of mobile charge are a sufficient but not necessary description of the dielectric loss observations, but the high conduction phenomenon lends further support to this idea of conducting channels with barriers in lossy diamonds. Such localized conducting channels would introduce inhomogeneities into an otherwise uniform electric field applied across an insulator. In bombardment conduction, measurements of counting efficiency could be very sensitive to field inhomogeneities.

Under alpha-particle bombardment a large variation in counting efficiency over the surface of typical diamonds is shown. In a group of 20 diamonds, most of those that exhibited definite losses also had high (≥ 25 percent) counting efficiencies in some region, and the majority of the remainder had low counting efficiencies. These experiments lend further support to the suggestion that inhomogeneous fields at least partially account for the inhomogeneities in bombardment conduction.

Serious errors in the normal estimates of range and mobility of electrons or holes in insulators can be introduced by neglecting these field inhomogeneities.

1. INTRODUCTION

IN studying the properties of diamond only the ideal valence bonded diamond structure which is perfectly periodic and perfectly uniform is usually considered. However, the literature contains many examples of inhomogeneities in the electrical and optical properties of diamond. They appear not only as variations from specimen to specimen but also as variations within small specimens.[1–6]

This paper reports experiments which show inhomogeneities in bombardment conduction and other electrical properties of diamond. When a potential difference is applied across a diamond of a given thickness one usually assumes that the field is the same at all points within the diamond. However, the experiments lead to the conclusion that in many diamonds this probably is not true; that on the contrary, the field may vary considerably from point to point. Consequently in certain regions, most of the potential drop may be localized within a distance small compared with the crystal thickness. In many cases this region where the potential drop is localized may be at or near the crystal surface. This paper presents the results of three different and independent experiments, none of which prove the validity of this conclusion but all of which strongly suggest that these field inhomogeneities frequently do occur. They are thought to be the result of an electrical conductivity that varies from region to region in the diamond.

2. DIELECTRIC LOSS EXPERIMENTS

2a. Introduction

The ideas that led to these experiments are as follows. Assume that the physical crystal contains lattice imperfections and chemical impurities and that they are not homogeneously distributed through the crystal. Wannier[7] and also James[8] showed that in an insulator, fluctuations in the height of the conduction and filled band relative to the Fermi level would be introduced by localized lattice imperfections. In extreme cases electrons would be introduced into the hollows of the conduction band or holes into the hills of the filled band depending on the sign of the charge of the imperfections. Thus there is the possibility of "pools of mobile charge" or "conducting channels" within the insulator and separated by barriers, and in the simplest case these channels and barriers could in turn be represented by a resistance R_s in series with a capacity C_s. Furthermore in an ac field, dielectric losses should appear and should depend on the frequency in a predictable way. The model of a series resistance and capacity R_s and C_s to represent the proposed conducting channels and barriers is equivalent to the parallel combination R_p and C_p (see Fig. 1) where R_p varies with the frequency f

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as follows.

$$R_p = R_s[1 + 1/(2\pi f R_s C_s)^2]. \quad (1)$$

This suggests measurements of dielectric loss in diamonds.

2b. Results

Typical results for one diamond are shown in Fig. 1. The experimental points give the measured values of R_p as a function of the frequency of the electric field. The data satisfy a straight line of slope -1.1 up to about 20 mc/sec. Above this frequency the vast majority of the points fall above this line indicating the approach of R_p to R_s which is independent of f. The dashed line represents Eq. (1) fitted to the experimental data. Considering the simplicity of the model represented by the dashed line, this fit is not bad. Perhaps the equivalent series resistance and capacitance consists of two or more such arrays with different time constants.

Losses like this were observed with about 13 out of a group of 20 diamonds studied. R_p at 70 mc/sec varied from 5×10^6 to 4×10^5 ohms. No losses[9] could be detected with the other 7 diamonds. Probe tests with some diamonds showed that at least a substantial part of the loss was localized within a small region of the crystal.

As most models of dielectric loss lead to a relation of this type, an explanation in terms of conducting channels and barriers is not unique. However, further experimental evidence presented in Sec. 3 suggests that this explanation is at least a reasonable one.

3. HIGH CONDUCTION EXPERIMENTS

3a. Introduction

The experimental support for the proposed conducting channels given by the dielectric loss measurements leads to the following possibility. Wannier and James pointed out that the aforementioned fluctuations in the band structure tend to be smoothed out when electron hole pairs are introduced as in photoconduction or bombardment conduction. This introduces the possibility that in this smoothing process a channel through the crystal might be established along which the conduction band approaches sufficiently to the Fermi level of the conducting electrode at the cathode insulator interface to allow electrons to pass from one electrode into the insulator crystal and out through the other.

This suggests that in extreme cases, a diamond crystal might pass a dc current far greater than that which is characteristic of the low intrinsic conductivity of diamond. Precisely this "high conduction" phenomenon was observed as described below.

3b. Results

In this section data and observations are presented on the high conduction current that appears in a few of

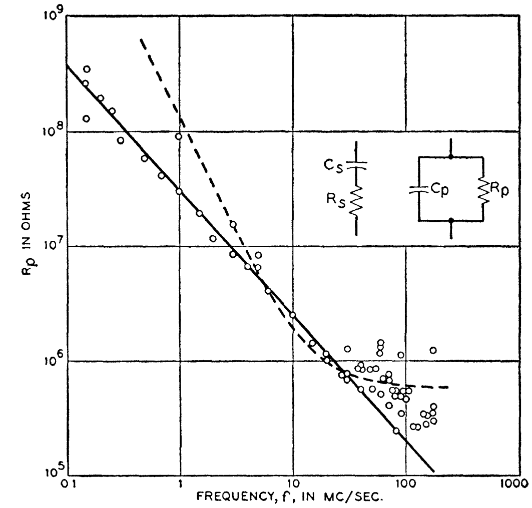

FIG. 1. Dielectric loss in diamond. Equivalent parallel resistance *vs* frequency of ac field.

the diamonds in which dielectric losses appear. Thus far this high conduction phenomenon has not been observed with diamonds in which no dielectric losses were observed. After a dc field of 10,000 to 20,000 volts/cm is applied to some of these lossy diamonds the resistance drops abruptly from the order of 10^{13} ohms to the order of a megohm. This occurs in some specimens even though they are in complete darkness. Once this high conduction current is initiated, it can be maintained with any specimen in complete darkness merely by maintaining a minimum field of several thousand V/cm.

Figure 2 shows how this high conduction current for a given diamond varies with the dc voltage. The points scatter widely. The current varies rapidly with voltage, dropping to zero at three to four hundred volts. Data for other diamonds are only qualitatively like this. For instance, in other specimens the current might persist to a lower voltage and might rise more rapidly or less rapidly with increasing voltage.

One of the characteristic features of this phenomenon is that while it appears abruptly there is a time lag or delay between the setting up of the necessary external conditions and this abrupt appearance. In some cases time lags of many minutes occurred. There is considerable variation in the amount and kind of external stimulation that is necessary to initiate high conduc-

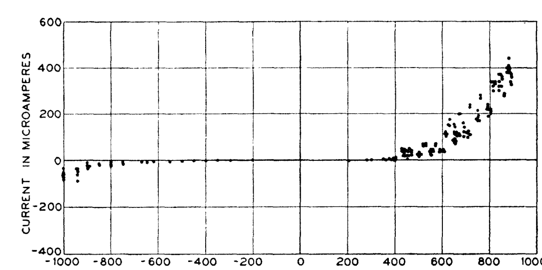

FIG. 2. High conduction in diamond. Dc current *vs* voltage.

[9] This indicates that negligible electrode losses are involved in these tests.

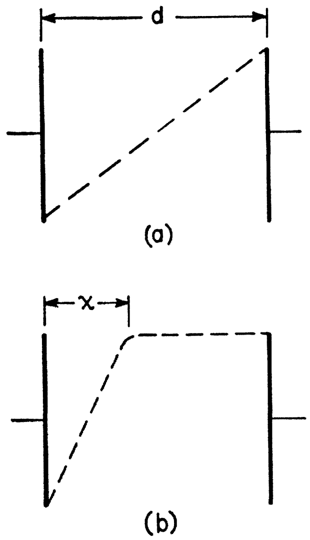

FIG. 3. (a) Potential drop uniformly distributed through insulator. (b) Potential drop concentrated near one surface.

tion. After the application of a field of 10,000 to 20,000 volts/cm, high conduction appears in some diamonds even though they are in total darkness. With other diamonds, bombardment with polonium alpha-particles or with white light while this field is applied, is necessary to establish this high conduction. With other lossy diamonds it was never observed. The time lags of many minutes already mentioned were observed under alpha-bombardment with a diamond in a high vacuum. This clearly demonstrates that we are dealing neither with a surface leakage nor a gas discharge. The time lag does suggest that an activation process is necessary to establish this dc conducting channel all the way through the crystal.

This high conduction current is not a case of dielectric breakdown since there appears to be no permanent change in the diamond. When the voltage is reduced to zero for more than a few seconds, the high conduction current does not reappear as soon as the voltage is turned on; it reappears only after the usual time lag.

This high conduction current is quite localized. This was first revealed by a minute fluorescent spot on the diamond and was later confirmed with a probe electrode. Many of the diamonds on which this report is based, have one or more internal cracks or flaws which in general, however, do not extend all the way through the specimen. In one specimen, this high conduction current was located at such an internal crack. With another specimen, it passed through a part of the diamond where no flaw could be detected at 200-fold magnification.

In the dielectric loss measurements, probe tests with some of the diamonds showed that at least a substantial part of the losses occur in the neighborhood of cracks in these stones. However, other specimens with prominent cracks were loss free.

4. ALPHA-BOMBARDMENT CONDUCTION EXPERIMENTS

4a. Introduction

The dielectric loss measurements lend support to the general idea of conducting channels with interspersed barriers. Furthermore, the measurements indicate that the series resistance R_s is as low as the order of a megohm. The high conduction experiments furnish additional support not only to the general idea of conducting channels but also to the megohm value by demonstrating that such values can be obtained sometimes in dc experiments. Now such localized conducting channels would introduce appreciable inhomogeneities in an electric field applied across a diamond.

The effect of these field inhomogeneities on measurements of bombardment conduction is shown in Fig. 3. In the usual analysis, a potential V applied to an insulator of thickness d is assumed to give the uniform field indicated by the potential distribution shown by the dashed line in the upper sketch in Fig. 3. When an electron is released by impact of an alpha-particle the conduction is determined by the range ω. The quantity measured by the amplifier is the normalized range Ω. It is proportional to the fraction of the anode cathode voltage that is traversed by the electron and is given by the relation

$$\Omega=\omega/d=\mu FT/d=\mu TV/d^2, \tag{2}$$

where μ is the mobility, F is the applied field, T is the free time in conduction band, and V is the potential applied.

Thus an electron released near the cathode must travel completely through the crystal to the anode in order to produce the optimum response in the amplifier.

Suppose now that in some region of this crystal there is one of the proposed conducting channels and

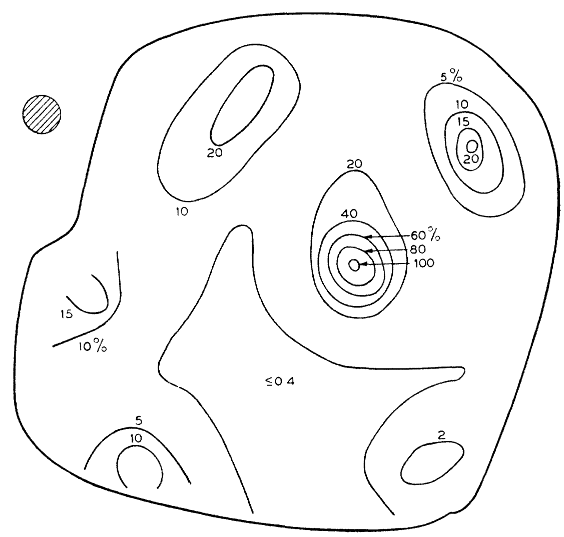

FIG. 4. Alpha-conduction in diamond. Counting efficiency inhomogeneities for electron pulses.

that in its neighborhood the potential distribution is altered to that indicated in the lower sketch of Fig. 3. Here most of the potential drop is localized in a layer of thickness x at the surface of the diamond. An electron released near the surface need only have a range ω equal to x in order to produce the optimum response in the amplifier. Moreover, in this region the field acting on the electron is substantially larger than in the above uniform field case. Consequently Eq. (2) becomes

$$\Omega=\omega/x=\mu TF/x=\mu TV/d^2(d/x)^2. \qquad (3)$$

Thus the quantity which the amplifier measures is magnified by the square of the factor d/x introduced by this field inhomogeneity. Therefore in alpha-bombardment conduction, a measurement of counting efficiency (in which all values of Ω above some preset value are registered) would be very sensitive to field inhomogeneities. It should be high when the field near the bombarded surface is high and when the field is low the counting efficiency should be low. This leads to measurements of counting efficiency in alpha-bombardment conduction, the details of which are described in the sections immediately following.

4b. Results

Some of the results were shown in Fig. 4. Here a diamond ($9B$) is manually scanned with a narrow beam of alpha-particles, the diameter of which is shown by the shaded disk. The contour lines show how the counting efficiency varies in different parts of the crystal. Here the electrode at the bombarded face is the cathode. Consequently the current pulses initiated by the alphas are electron pulses.

These scanning experiments revealed a wide range of counting efficiencies. In Fig. 4 the values vary from zero to 100 percent. With only minor exceptions, the same relative peaks and valleys of Fig. 4 appeared in the same positions when positive hole pulses were counted. The spread in this case was from zero to 71 percent. Figure 4 clearly demonstates that the over-all response is largely contributed by a very localized area. A large internal crack is located in this region of the diamond and it is here that the dielectric loss and high conduction current are located.

Variations in counting efficiency like those shown in Fig. 4 are not exceptional; they are the general rule. Field inhomogeneities could constitute an important factor[10] in accounting for these variations by assuming that the peaks of high counting efficiency are regions where the field is high and that at the region of zero counting efficiency the field is very low.

Measurements of counting efficiency and dielectric loss on about twenty diamonds are shown in Fig. 5. The value plotted on the ordinate is that of the highest

[10] Inhomogeneities in the density of electron traps or positive hole traps may still be an important factor influencing counting efficiency variations.

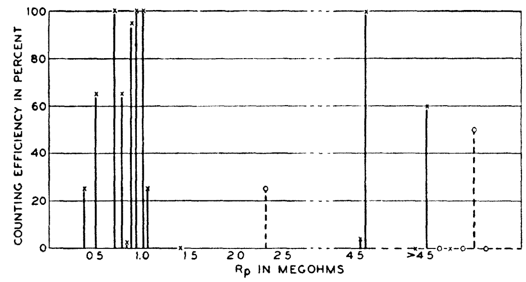

FIG. 5. Alpha-conduction in diamond. Counting efficiency *vs* equivalent parallel resistance. (× measured C.E., 0 estimated C.E.)

counting efficiency region of the diamond. On the abscissas R_p the equivalent parallel resistance calculated from the dielectric loss measurements at 70 mc/sec is plotted. The smallest loss that could be detected in these experiments corresponds to $R_p=5\times10^6$ ohms approximately. Consequently the points to the right of this value are for diamonds in which no loss was observed.

The large majority of the diamonds showing measurable losses have a relatively high counting efficiency. Similarly the large majority of those that show no dielectric loss have zero counting efficiency. Among the lossy diamonds an enhanced field could account for the high counting efficiency cases and a depressed field could explain the low ones. Among the diamonds with which losses were not detected there are a couple of exceptions to the general rule of zero counting efficiency. This probably indicates another factor favorably affecting the bombardment conduction in these cases. The over-all correlation between losses and counting efficiency suggests that inhomogeneous fields occur and account at least in part for these observed counting efficiency variations, variations that appear not only from specimen to specimen but also in different parts of a given specimen.

F. FIELD INHOMOGENEITIES AND MEASUREMENTS OF RANGE AND MOBILITY IN DIAMOND

None of these experiments on dielectric loss, high conduction and bombardment conduction prove the existence of the proposed field inhomogeneities but all of them suggest that such inhomogeneities do frequently occur in diamond. Such field variations would have an important influence on determinations of the numerical values of the range ω and the mobility μ of electrons or holes in insulators like diamond. This is best shown by referring to Fig. 3 and Eqs. (2) and (3) of Sec. 4. In the homogeneous field case shown in Fig. 3 a calculation of range ω using Eq. (2) would be in error by the factor $(d/x)^2$. Thus serious errors in the normal estimates for the values of range and mobility of electrons and holes in insulators can be introduced by neglecting these field inhomogeneities.

6. SUMMARY

1. Inhomogeneities, particularly in electrical properties, are common in diamond.
2. Dielectric losses are frequently observed in diamond.
3. The phenomenon of high conduction is observed with some but not all lossy diamonds and is not observed with loss free diamonds.
4. The dielectric losses and high conduction suggest that conducting channels frequently occur. Such channels would introduce inhomogeneities in an electric field applied across an insulator.
5. In alpha-bombardment conduction the variation in counting efficiency in different regions of a given diamond are readily explained in terms of field inhomogeneities.
6. Most diamonds that exhibit definite losses have a high counting efficiency in some region. Most of the loss free diamonds have very low counting efficiencies. This suggests that inhomogeneous fields at least partially account for variations in bombardment conduction.
7. Serious errors in the normal estimates of range and mobility of electrons or holes in insulators can be introduced by neglecting these field inhomogeneities.

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Experiments with Audiofrequencies on Superconductors*

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Experiments are described in which alternating and direct currents are superimposed on tin wires in the superconducting state. As the amplitude of the ac is increased, the average PD goes through a maximum and approaches an asymptotic value. The experimental curves agree with calculated curves for low frequency ac (<50 cycles/sec). However, as the frequency is increased the curves change in character. The maxima increase in height and occur at large values of the ac. It is shown that this anomalous behavior can be traced to the ac skin effect, and it is concluded that experiments of this type are not suitable for a determination of the relaxation time in the phase transition from the superconducting to the normal states.

1. INTRODUCTION

LAZAREV, Galkin, and Khothevich[1] have studied the behavior of thallium wires carrying high frequency alternating currents of such amplitude as to induce a phase transition between the superconducting and the normal states. The general concept of the experiment is found in the earlier work of Silsbee, Brickwedde, and Scott.[2] It consists in superimposing direct and alternating currents on a superconductor and measuring the average potential difference as a function of the amplitude of the ac. Lasarev and co-workers believed that a study of this relationship at low and at high frequencies could be used to determine the relaxation time in the phase transition of a superconductor. Recently, Pippard[3] has shown theoretically that it is reasonable to expect that the kinetics of the phase transition is basically governed by the electromagnetic effects accompanying the penetration of the magnetic field into the normal conducting metal.

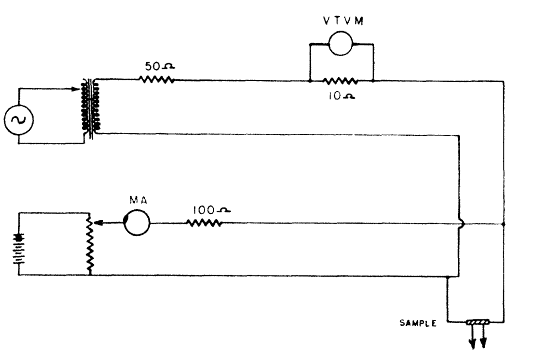

Fig. 1. Measuring circuit.

We have repeated the experiments of Lasarev *et al.*, with tin wires and have found that at quite low frequencies the electromagnetic effects, which can be represented by the usual ac skin penetration, greatly influence the experimental results, thereby making dubious an interpretation in terms of a relaxation time. The bulk of this paper is devoted to presenting the

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