

## High-temperature thermal conductivity of electron-irradiated diamond

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The damage in diamond produced by electrons of 0.60, 0.90, and 1.50 MeV was found to give a reduction of the thermal conductivity between 320 and 450 K. The damage was stable upon annealing to about 800 K. For type-IIa diamond the radiation-induced thermal resistivity  $R(T)$  equals  $2.4 \times 10^{-21} n_V \text{ W}^{-1} \text{ cm K}$  at 320 K and  $1.7 \times 10^{-21} n_V \text{ W}^{-1} \text{ cm K}$  at 450 K, where  $n_V$  denotes vacancy concentration. This conclusion was reached by taking the displacement energy of carbon atoms to be 80 eV, by assuming no instantaneous recombination, and by neglecting any effect of displaced atoms on the high-temperature thermal conductivity. For type-I diamond, larger values were found for  $R(T)$ , suggesting that displaced carbon atoms might be trapped on the nitrogen impurity. The results for irradiated type-IIa diamond and unirradiated type-I diamond indicate that vacancies cause somewhat more strain in the lattice than nitrogen. For these two kinds of point defects there was also a difference in the temperature dependence of the thermal conductivity.

### I. INTRODUCTION

The optical, electrical, and paramagnetic properties of irradiated diamonds have been investigated by previous workers to obtain knowledge of the damage processes.<sup>1</sup> It has been found that electron irradiation produces vacancies which do not migrate until 1125 K and displaced carbon atoms which are mobile at room temperature.<sup>2</sup> Apparently only one thermal-conductivity study of irradiated diamonds has been reported. This was at low temperatures (1–20 K) by Vandersande.<sup>3</sup> The present thermal-conductivity measurements were made at much higher temperatures (320–450 K). The interpretation of irradiation effects in diamond is rather different in these two temperature ranges. The thermal conductivity at low temperature is mainly determined by phonon scattering at crystal boundaries and large defects, whereas point defects are dominant at higher temperatures. Accordingly, Vandersande's experiment was interpreted in terms of clustered interstitials and ours as a function of vacancy concentration.

The conversion from dose to vacancy concentration depends on the displacement energy of carbon atoms in diamond, called  $E_d$ . It was inferred from the optical absorption produced at or above room temperature<sup>4</sup> that  $E_d = 80$  eV. The change in electrical resistance produced by irradiations at low temperature indicated<sup>5</sup> that  $E_d = 35$  eV, and this value is rather close to the theoretical one.<sup>5,6</sup> This disagreement on  $E_d$  values was attributed in Ref. 2 to the existence of a defect which anneals below room temperature. Thus, the value of 80 eV seems to be valid for our study and electrons

of about 1 MeV produce then single vacancies.<sup>6</sup> The analysis of the effect of irradiation on the thermal conductivity is more straightforward for single vacancies than for multiple defects produced by electrons of much higher energies or by ion and neutron irradiations.

The analytical treatment of phonon scattering in diamond worked out by Turk and Klemens<sup>7</sup> can be used for diamonds containing vacancies. However, the scattering caused by the local strain associated with a vacancy is important and not easily calculable. This makes a theoretical estimate of the effect of electron irradiation on the thermal conductivity very difficult. However, the measurements of the thermal conductivities of irradiated diamonds can be used conversely to yield an estimate of the strain.

At temperatures slightly above room temperature, point-defect scattering in diamond is more important than in other solids. Thus the effect of irradiation on the high-temperature thermal conductivity will be larger in diamond than in other solids. It might even be unique for diamond, because it also seems that vacancies in diamond are stable around room temperature, and this is in contrast to most other solids.

### II. EXPERIMENTS

The diamonds of this study are rectangular bars free from cracks and inclusions at 20× magnification. The diamonds are listed in Table I; those with serial numbers were used in Ref. 8. Diamond no. 48 is a type-IIb diamonds and nos. 84 and 86 are type-I diamonds with different kinds of in-

TABLE I. Thermal conductivities  $k^u(T)$  and  $k^i(T)$  of unirradiated and irradiated diamonds. The main error is in the conductivity values and is about 5%.

Diamond no.	$k^u(320)$ (W cm <sup>-1</sup> K <sup>-1</sup> )	$k^u(450)$ (W cm <sup>-1</sup> K <sup>-1</sup> )	Energy (MeV)	Total dose (10 <sup>19</sup> e/cm <sup>2</sup> )	$k^i(320)$ (W cm <sup>-1</sup> K <sup>-1</sup> )	$k^i(450)$ (W cm <sup>-1</sup> K <sup>-1</sup> )
1	20.2	12.3	1.50	0.31	16.7	11.1
3	19.0	12.5	1.50	1.87	10.3	8.6
4	19.0	12.5	1.50	0.94	13.5	10.3
6	19.1	12.6	1.50	1.25	13.2	10.9
8	19.8	11.8	1.50	3.12	9.5	7.9
8			1.50	5.62	7.4	7.0
18	19.2	12.7	1.50	1.25	13.2	10.9
18			1.50	4.37	8.3	7.4
18			1.50	5.77	6.9	6.8
18			1.50	8.27	5.0	5.6
25	19.4	12.5	1.50	2.50	9.8	8.5
48	20.1	11.7	1.50	0.31	16.7	11.7
84	8.3	6.3	1.50	3.12	3.5	3.7
86	7.6	5.9	1.50	3.12	3.0	3.7
a and b	19.0	12.7	0.90	2.50	12.4	9.9
c	20.4	13.0	0.60	2.50	15.4	11.2
d	19.6	11.9	0.60	5.31	11.5	9.5

frared absorption.<sup>8</sup> The other diamonds, including a, b, c, and d, are of type IIa and were selected on the basis of transparency above 7- $\mu$ m wavelength and electrical resistivity higher than 10<sup>12</sup>  $\Omega$  cm.

The irradiations of these diamonds were with electrons from a Van de Graaff accelerator. A few diamonds (generally 4 mm long and 1 mm wide) were mounted normally to the electron beam. Diamonds of 1.00-mm thickness were irradiated in several runs with electrons of 1.50 MeV. Diamonds of 0.50- and 0.30-mm thickness were used for irradiations with electrons of 0.90 and 0.60 MeV, respectively. The thicknesses were only about half the range of the electrons<sup>6</sup> and this implies that the defect production is nearly homogeneous. Moreover, the diamonds were irradiated for the same time on each of two opposite sides.

It was estimated that the temperature of diamonds nos. 6 and 18 was 330 K during the first run. In the other runs the temperature of the diamonds was always less than 500 K. The electron flux was measured with a Faraday cup and was  $4.8 \times 10^{17}$  cm<sup>-2</sup> h<sup>-1</sup> during the first run and about  $7 \times 10^{18}$  cm<sup>-2</sup> h<sup>-1</sup> in the other runs.

In order to determine the thermal conductivity  $k$ , a steady heat flow was set up in the direction of the length of a diamond bar, and the temperature gradient was measured with radiation thermometry. Details of the method are given in Ref. 8. Figure 1 shows the results for diamond no. 18 as an illustration of the experiment. Values of  $k$  at 320 and 450 K were derived for each set of measurement points by means of

$$k \propto T^s. \quad (1)$$

The results for unirradiated and irradiated diamonds are denoted as  $k^u(T)$  and  $k^i(T)$ , respectively, and are given in Table I.

The thermal-conductivity values for the irradiated diamond no. 6 were measured first below 330 K, then up to 500 K and subsequently below 330 K

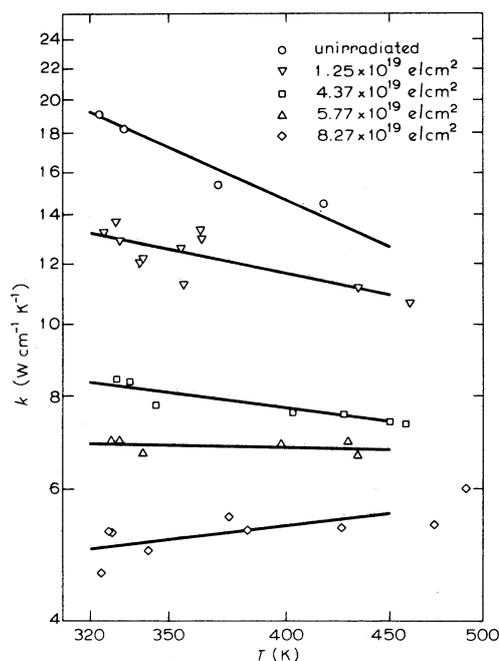


FIG. 1. Measured thermal conductivity of diamond no. 18 before and after several irradiations with 1.50-MeV electrons.

again. Since the values below 330 K were found to be equal, it was concluded that significant annealing of defects does not occur below 500 K and that temperatures up to 500 K could be allowed during irradiations and thermal-conductivity measurements. Furthermore, it was found on remeasurement of some irradiated diamonds after one year that the conductivity had not changed. Thus it seems that the damage is stable in diamond stored at room temperature.

The effect of annealing of the damage was explored at temperatures above 500 K for three diamonds. They were stepwise annealed in a vacuum for one hour at temperatures up to 1600 K. The thermal conductivities were measured after each anneal step and the results, derived by means of Eq. (1) and denoted as  $k^a(T)$ , are listed in Table II.

The color of all the irradiated diamonds was light to very dark blue, depending on the dose. The annealing experiments showed that the color changes via green to red-brown around 1000 K and to a smoky color above 1300 K. The relatively low dose of diamond no. 48 caused the electrical resistivity to change from  $10^2$  to  $10^6 \Omega \text{ cm}$  and the specific infrared absorptions of type-IIb diamond (for instance, at  $3.56 \mu\text{m}$ ) to disappear. The irradiation of diamonds nos. 84 and 86 induced a narrow absorption peak at  $6.90\text{-}\mu\text{m}$  wavelength with a strength of about  $12 \text{ cm}^{-1}$ . This peak was

TABLE II. Thermal conductivity  $k^a(T)$  of diamonds which have been annealed after irradiation.

Diamond	Anneal temp. (K)	$k^a(320)$ ( $\text{W cm}^{-1} \text{K}^{-1}$ )	$k^a(450)$ ( $\text{W cm}^{-1} \text{K}^{-1}$ )
no. 6 (irradiated with $1.25 \times 10^{19} \text{ e/cm}^2$ )	500	13.2	10.9
	575	13.2	10.6
	775	13.1	11.0
	875	14.0	11.3
	975	14.8	11.4
	1075	16.3	11.8
	1175	15.7	11.6
	1275	16.2	12.1
	1400	16.1	11.9
	1600	16.9	11.8
no. 8 (irradiated with $5.62 \times 10^{19} \text{ e/cm}^2$ )	500	7.4	7.0
	600	7.5	7.0
	825	7.4	6.9
	950	8.1	7.7
	1050	10.2	8.8
	1400	13.7	10.7
	1600	15.0	11.2
no. 86 (irradiated with $3.12 \times 10^{19} \text{ e/cm}^2$ )	500	3.0	3.7
	1075	5.9	5.4
	1400	6.4	5.4

not observed in the other diamonds. No other effects of irradiation on infrared absorption between  $2.0$  and  $9.5 \mu\text{m}$  were observed.

### III. DISCUSSION

#### A. Effect of dose

A thermal resistivity

$$R(T) = \frac{1}{k^1(T)} - \frac{1}{k^a(T)} \quad (2)$$

is defined for analysis. Values  $R(320)$  and  $R(450)$  were calculated from the data of Table I and plotted in Fig. 2 for type-IIa diamonds irradiated with  $1.50\text{-MeV}$  electrons. Regression lines through these values and the origins are shown. The difference in slope of these lines indicates that the effect of dose is smaller at higher temperatures as was obvious in Fig. 1. Diamonds nos. 18 and 8 were irradiated in several runs and calculation of the differential dose and corresponding  $R(T)$  values give results in agreement with the lines in Fig. 2.

The results of the irradiated type-IIb diamond would also fit these lines satisfactorily, but those for the two type-I diamonds would lie far above the lines (see also Sec. III E). The  $R(T)$  values of diamonds irradiated with electrons of  $0.90$  and  $0.60 \text{ MeV}$  would lie considerably below the lines. Comparison of the thermal resistivities for the various electron energies requires conversion from dose to damage.

#### B. Thermal resistivity versus vacancy concentration

The observed reduction of the thermal conductivity of type-IIa diamond is attributed to vacancies. Displaced carbon atoms give negligible effect on the high-temperature thermal conduc-

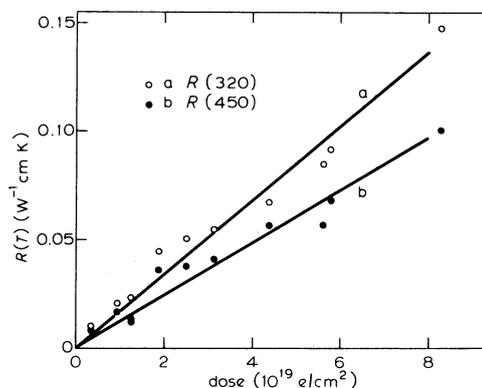


FIG. 2. Radiation-induced resistivity for type-IIa diamonds irradiated with  $1.50\text{-MeV}$  electrons. Line a is a fit to the open circles representing  $R(320)$  values and line b is a fit to the black ones for  $R(450)$ .

tivity since they are at interstitial positions. Moreover, because of their mobility, they will diffuse through the crystal until they are trapped on impurities. They might also be clustered.<sup>3</sup> Extended impurities or large clusters are not effective scatterers above room temperature. The number of vacancies per  $\text{cm}^3$   $n_V$  is given by the product of dose, displacement cross section, and the number of carbon atoms per  $\text{cm}^3$   $n_C$ . The value of the displacement cross section  $\sigma_d$  depends on the displacement energy of carbon atoms  $E_d$  and on the energy of the electrons  $E_e$ .

Mitchell has calculated  $\sigma_d$  for various  $E_d$  and  $E_e$  values.<sup>5</sup> An interpolation of his data yields for  $E_d = 80$  eV that  $\sigma_d$  is  $1.78 \times 10^{-24}$  or  $2.75 \times 10^{-24}$   $\text{cm}^2$  when  $E_e$  is 0.60 or 0.90 MeV, respectively. At these energies there is only primary damage. The value of  $\sigma_d$  is  $4.03 \times 10^{-24}$   $\text{cm}^2$  when  $E_e = 1.50$  MeV, and in this case about 7% of the vacancies are produced secondarily by displaced carbon atoms. These include both divacancies and single vacancies, and the effect of divacancies can thus be neglected. Lowering of the  $E_d$  value gives more increase of the  $\sigma_d$  value for low electron energies than for high electron energies. For instance, for  $E_d = 35$  eV the values of  $\sigma_d$  are  $9.4 \times 10^{-24}$ ,  $11.0 \times 10^{-24}$ , and  $13.8 \times 10^{-24}$   $\text{cm}^2$  when  $E_e = 0.60$ , 0.90, and 1.50 MeV, respectively.

Using the above  $\sigma_d$  values, the lines *a* and *b* of Fig. 2 were converted to Fig. 3, where they represent our mean results for 1.50-MeV electrons. In the case of  $E_d = 80$  eV, the  $R(320)$  values found for 0.60- and 0.90-MeV electron irradiations lie slightly below the line *a*. The results for  $R(450)$  are similar (black symbols should be compared to line *b* only). There is satisfactory agreement between the results in the left part of Fig. 3. However, if  $E_d < 80$  eV had been used, the  $R(T)$  values for  $E_e = 0.60$  or 0.90 MeV would have lain further below the 1.50-MeV lines. This is shown in the right part of Fig. 3 as an example for  $E_d = 35$  eV.

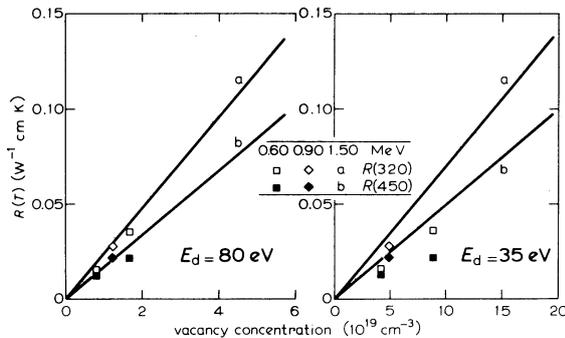


FIG. 3. Radiation-induced resistivity for type-IIa diamonds irradiated with electrons of various energies vs the vacancy concentration derived for  $E_d = 80$  and 35 eV.

Our irradiations with electrons of various energies support thus the value  $E_d = 80$  eV.

The results in the left part of Fig. 3 can be expressed by  $R_V(320) = 2.4 \times 10^{-21} n_V$  and  $R_V(450) = 1.7 \times 10^{-21} n_V$   $\text{W}^{-1} \text{cm K}$ . Although the damage was found to be stable after the irradiation, it is possible that during the irradiations ionized displaced atoms and charged vacancies recombine more easily than in the neutral state. This instantaneous recombination is important in irradiation at low temperature<sup>2</sup> and might be still of some importance in our analysis. Although other instantaneous-recombination mechanisms can also be present, the expressions of  $R_V(T)$  vs  $n_V$  are based on an assumption of negligible instantaneous recombination.

### C. Comparison of diamonds containing vacancies with those containing nitrogen

The thermal conductivity of diamond above room temperature is determined by umklapp processes and by phonon scattering on point defects such as <sup>13</sup>C isotopes, impurity atoms, and vacancies. Umklapp processes and isotope scattering do not vary among diamonds,<sup>9</sup> in contrast to scattering on impurity atoms and vacancies which depends on the concentrations. The Turk and Klemens equation<sup>7</sup> for point-defect scattering may be generalized to

$$R \propto n \left( \frac{\Delta M}{2M} + P \right)^2, \quad (3)$$

where  $n$  represents concentration of impurity atoms or vacancies,  $\Delta M$  is the mass difference between impurity atoms or vacancies and carbon atoms of mass  $M$ , and  $P$  is a parameter for the strain associated with impurities or vacancies.

The concentrations of impurities in unirradiated type-IIa and -IIb diamond are too low to affect the thermal conductivity above room temperature.<sup>8</sup> However, type-I diamonds contain nitrogen<sup>10</sup> in such high concentrations [up to 0.5 at. % (Ref. 11)] that impurity scattering is very important over a wide temperature range.<sup>8,9,12</sup> It can be inferred from Refs. 8 and 12 that  $R_N(320) \sim R_N(450) \sim 0.3 \times 10^{-21} n_N$   $\text{W}^{-1} \text{cm K}$ . We ignore here the fact that nitrogen can be present in several forms in the diamond: commonly pairs of nitrogen atoms replace pairs of carbon atoms. The value of  $P_N$  would be about 0.3 according to Refs. 7 and 9. The results for nitrogen yield the constant of proportionality in Eq. (3). This constant in turn and the relations between resistivity and vacancy concentration (Sec. III B) lead to  $P_V = -0.5$  or  $+1.5$ . The minus sign corresponds to movement of the four neighboring carbon atoms toward the vacancy as is predicted by theoretical calculations.<sup>13,14</sup> The

value  $P_v = -0.5$  indicates that vacancies cause somewhat more strain in the lattice than nitrogen atoms.

It should be stressed that the above  $P_v$  value is only an estimate, since, apart from the use of some approximate values, Eq. (3) is based on the Debye approximation, which is a simplification in our temperature range. Moreover, we have ignored the temperature dependence of the thermal resistivity which is not the same for the two kinds of point defects. This is shown in Fig. 4, where all thermal-conductivity data at 320 K (Tables I and II) have been plotted against the  $s$  values [Eq. (1)]. There is one trend of results for all irradiated diamonds including the type I's and those irradiated with 0.90- and 0.60-MeV electrons. This trend is shown in Fig. 4 as a band marked with  $V$ . The results for the unirradiated type-I diamonds lie significantly below this trend. They fit another trend which was given in Fig. 3 of Ref. 8 and was found for 49 unirradiated type-I diamonds. This trend is indicated in Fig. 4 with  $N$ . The existence of different trends of  $s$  values for diamonds containing vacancies and diamonds containing nitrogen is significant and indicates that these two kinds of point defects are not equivalent in terms of Eq. (3).

Figure 4 shows that annealing of irradiated type-II diamonds does not give departure from the trend for irradiated diamonds. This may indicate that vacancy clustering does not occur upon annealing.

#### D. Isochronal-annealing experiment

A few diamonds were annealed after irradiation, and the results  $k^a(T)$  are shown in Table II. A thermal resistivity after the anneal is defined as

in Eq. (2),

$$R^a(T) = \frac{1}{k^a(T)} - \frac{1}{k^u(T)}. \quad (4)$$

We then define

$$r(T) = \frac{R^a(T)}{R(T)}, \quad (5)$$

where  $R(T)$  refers to the resistivity when the diamond was kept below 500 K, as in Secs. IIIA-III C. The results derived for the two type-II diamonds have been plotted in Fig. 5 versus the anneal temperature. The  $r$  values for the annealed type-I diamond would lie far below these results.

The curve in Fig. 5 is an empirical fit to the experimental results and is not based on any model for recombination of vacancies and displaced carbon atoms. First-order annihilation would give curves with more steplike shapes. The results at 320 and 450 K are in agreement. Apart from some systematic scatter at the highest temperatures, the results for the two diamonds with a low and a high irradiation dose agree satisfactorily. The defects in both diamonds appear to be stable up to about 800 K and this justifies the allowance of a maximum temperature of 500 K during the experiments. Since vacancy migration is thought<sup>2</sup> to start around 1125 K, detrapping of displaced carbon atoms may account for vacancy annihilation starting around 800 K.

#### E. Results for irradiated type-I diamonds

$R(T)$  values determined via Eq. (2) from Table I have been tabulated in Table III. The  $R_v(T)$  values have been derived from the irradiation dose via Fig. 2. Since these values are considerably smaller than the  $R(T)$  values, it is assumed that

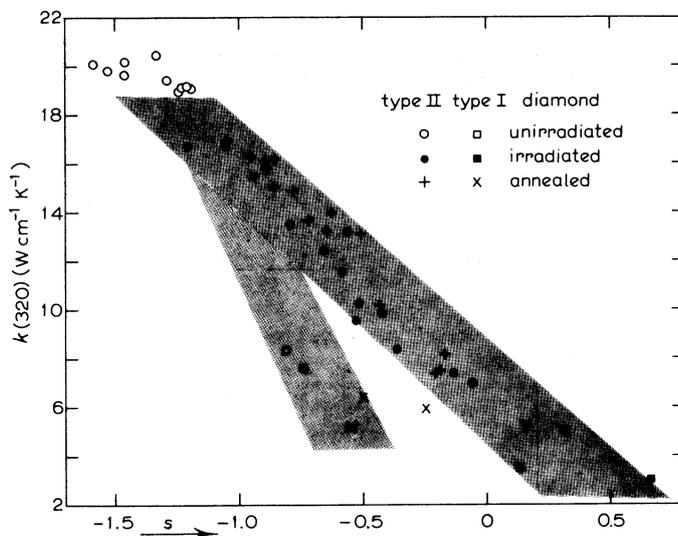


FIG. 4. Thermal conductivity at 320 K against the slope defined in Eq. (1) for all diamonds measured (see Tables I and II). Two trends for results of diamonds containing vacancies and diamonds containing nitrogen are shown with  $V$  and  $N$ .

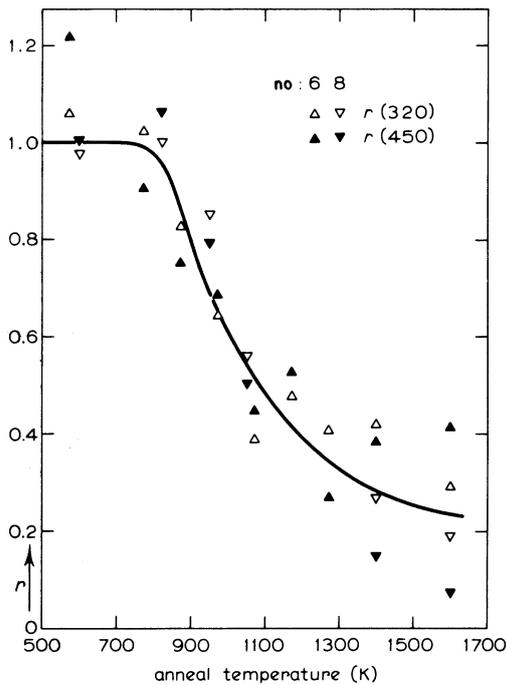


FIG. 5. Normalized resistivity against the temperature at which the two diamonds were annealed (one hour at each temperature).

$$R(T) = R_V(T) + R_I(T). \quad (6)$$

The term  $R_I(T)$  represents a specific effect of irradiation in a type-I diamond, and  $R_V(T)$  is associated with the vacancies produced in the same way as in a type-IIa diamond. The anneal experiments with diamond no. 86 (Table II) give on average  $R^a(320) = 0.03$  and  $R^a(450) = 0.02$   $\text{W}^{-1} \text{cm K}$ . These values correspond rather well with the results for irradiated type-IIa diamonds which were annealed above 1075 K. Therefore, the term  $R_I(T)$  appears to decrease to zero upon annealing.

Phonon scattering on nitrogen point defects in unirradiated type-I diamonds gives rise to a thermal resistivity

$$R_N(T) = \frac{1}{k''(T)} - \frac{1}{k_{IIa}(T)}. \quad (7)$$

The mean thermal conductivities of the type-IIa diamond were reported in Ref. 8 and are  $k_{IIa}(320)$

$= 19.3$  and  $k_{IIa}(450) = 12.5$   $\text{W cm}^{-1} \text{K}^{-1}$ . The values of  $R_N(T)$  are listed in Table III. They are smaller than the  $R(T)$  values, indicating that for the irradiated type-I diamonds nitrogen scattering is not dominant. Therefore, there is one trend for irradiated diamonds in Fig. 4, both for type I and type II's. On the other hand,  $R_N(T)$  values are larger than  $R^a(T)$  values, and thus after annealing the nitrogen scattering becomes dominant. This is consistent with the position of the  $\times$  symbols in Fig. 4.

The experiments indicate that the thermal conductivity of irradiated type-I diamonds is determined by three additive point-defect scattering terms. One is caused by nitrogen atoms, one by vacancies, and one by an effect of irradiation in the type-I diamond. The latter term is most probably caused by trapping of displaced carbon atoms on nitrogen atoms. Detrapping upon annealing causes the term  $R_I(T)$  to decrease. The value of this term depends perhaps on the form of nitrogen in the diamond. The mechanism responsible for the term  $R_I(T)$  might be associated with the irradiation-induced infrared absorption at  $6.90$   $\mu\text{m}$  (Sec. II). Runciman and Carter<sup>15</sup> observed this absorption also only in a type-I diamond. A peculiar point, however, is that the absorption does not disappear upon annealing whereas  $R_I(T)$  decreases to zero.

#### IV. CONCLUSIONS

Irradiation of diamond with fast electrons gives damage which can be observed as a reduction of the thermal conductivity. For the type-IIa diamond irradiated with 1.50-MeV electrons it was found that the thermal resistivity associated with this reduction depends linearly on the dose. The resistivity is thus also proportional to the vacancy concentration, since displaced carbon atoms give negligible effect on the thermal conductivity of a type-IIa diamond above room temperature. Irradiations with electrons of 0.90 and 0.60 MeV lead to results in agreement with those for 1.50-MeV electrons, if a value of 80 eV is used for the displacement energy and if it is assumed that there is no instantaneous recombination.

Comparison of the results for irradiated type-IIa

TABLE III. Radiation-induced resistivity  $R(T)$  for Type-I diamonds compared to the resistivities  $R_N(T)$  and  $R_V(T)$  attributable to nitrogen and vacancies.

Diamond no.	$R(320)$ ( $\text{W}^{-1} \text{cm K}$ )	$R(450)$ ( $\text{W}^{-1} \text{cm K}$ )	$R_V(320)$ ( $\text{W}^{-1} \text{cm K}$ )	$R_V(450)$ ( $\text{W}^{-1} \text{cm K}$ )	$R_N(320)$ ( $\text{W}^{-1} \text{cm K}$ )	$R_N(450)$ ( $\text{W}^{-1} \text{cm K}$ )
84	0.16	0.11	0.053	0.038	0.07	0.08
86	0.21	0.10	0.053	0.038	0.08	0.09

diamonds and unirradiated type-I diamonds gave an estimate for the strain around vacancies in the lattice. The temperature dependence of the conductivity of diamonds containing vacancies was found to differ from that of diamonds containing nitrogen. The radiation-induced resistivity was not affected by annealing at temperatures up to 800 K. Above this temperature it decreased until

at 1600 K the conductivity was restored to a value approaching that of unirradiated diamond. Radiation induced a larger thermal resistivity in type-I diamonds than in type-IIa diamonds.

#### ACKNOWLEDGMENT

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