

Thermal-conductivity reduction in electron-irradiated type-IIa diamonds at low temperatures

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The low-temperature thermal conductivity of three type-IIa diamonds irradiated with 0.75-MeV electrons at room temperature and one irradiated at 77 K was found to be reduced and is characteristic of phonon scattering by large aggregates: the conductivity changing from Rayleigh scattering at the lowest temperatures to geometrical scattering at higher temperatures. The size and concentration of these irradiation-produced aggregates were determined by fitting a theoretical model to the experimental results. Calculations based on the number of displaced atoms and on the number needed to form aggregates show that the formation of aggregates is possible but that the aggregates are limited to certain shapes and densities. The results indicate that the interstitial in diamond becomes mobile at a temperature between 77 K and room temperature in agreement with the recent suggestion of Lomer and Wild.

I. INTRODUCTION

During the past decade several research groups¹⁻³ have studied the low-temperature thermal conductivity of alkali halides containing colloidal precipitates. The size and concentration of these colloids were determined from the shape of the conductivity curve and from theoretical models which were used to fit this curve. This work was extended to study γ -irradiated alkali halides and it was found that clusters (aggregates) had been formed as a result of the irradiation. A plot of the thermal conductivity of electron-irradiated type-IIa diamonds is similar in shape to the conductivity of the alkali halides containing colloids and aggregates. This similarity together with additional experimental results reported here have led to the conclusion that aggregates are also formed in irradiated diamonds. However, this is contrary to the current belief that only Frenkel pairs are formed in irradiated diamonds and that the interstitial is not mobile at the irradiation temperature (room temperature).

For diamond there is little evidence for the temperature of mobility of both interstitials and vacancies. The interstitial has up until a few years ago been correlated with the C system (three pairs of lines having $\langle 100 \rangle$ symmetry axis) in the ESR spectrum. This system has only been found after irradiation and was found to anneal out completely between 350 and 450 °C.⁴ Lomer and Wild,⁵ with ESR measurements on IIa diamonds electron irradiated at low temperatures, have shown that during irradiation centers are produced which anneal below room temperature. It is suggested by them that this center is the interstitial and this would thus be evidence that the interstitial is mobile below room temperature. This led Clark

and Mitchell⁶ to conclude that it is difficult to maintain that the C system can be associated with isolated interstitials and that 450 °C is much too high to correspond to the onset of interstitial mobility.

The vacancy has been correlated with the so-called GR1 band which is centered at about 2 eV in optical absorption and has only been found after irradiation.⁷ Since this band only starts annealing out at 350–450 °C it was concluded that the vacancy is immobile at room temperature and only becomes mobile well above it. This GR1 band is only totally annealed out at 950 °C. Only the uv experiments on annealed, electron irradiated type-IIa diamonds by Clark, Ditchburn, and Dyer⁸ seem to indicate the possible presence of aggregates. They compared the uv spectra of IIa diamonds annealed at 850 °C for 21 h with the spectra taken before the irradiation and observed a uniform increase in absorption over the range of the uv absorption tail (from 1.5 eV to the edge at 5.4 eV). From this they suggested that the residual crystal-line disorder is probably due to thermally stable aggregates of interstitials or vacancies.

The number of previous studies of unambiguous phonon scattering by precipitates or colloids or aggregates, as they will be referred to here, is small.

Worlock⁹ measured the thermal conductivity of NaCl crystals containing silver colloids down to 1.2 K. He was the first to note and emphasize the very strong scattering strength of precipitates. A concentration of 10^{13} colloids per cm^3 reduced the conductivity by about half. At the lowest temperatures the conductivity was proportional to T^3 while being considerably below the Casimir value. This indicated that down at low temperatures the scattering from the aggregates appeared to be in-

dependent of phonon frequency.

Walton,¹ using the same crystals, extended the measurements down to 0.2 K. By going to lower temperatures he was able to observe the transition from a geometrical scattering law, when the phonon wavelength is less than the size of the colloids, to a Rayleigh scattering law, when the phonon wavelength is larger than the colloid dimensions.

Schwartz and Walker² measured the thermal conductivity of quenched and annealed KCl and KBr containing Ba⁺⁺ and Sr⁺⁺ over the temperature range of 0.35–10 K. Their quenched crystals had a conductivity which one would expect for phonon scattering by precipitates about 100 Å in size, being Rayleigh like at the lowest temperatures and geometrical at higher temperatures. Both Walton¹ and Schwartz and Walker² fitted their experimental results with a theoretical model and showed that the lattice thermal conductivity could be used to measure the sizes of inclusions (aggregates) in crystals.

Guenther and Weinstock³ measured the thermal conductivity of γ -irradiated KCl from 0.2 to 4 K and measured several samples irradiated at room temperature and at liquid-nitrogen temperature. They also fitted the experimental results with a theoretical model and obtained evidence for interstitial aggregates with a radius of about 70 Å in the room-temperature irradiated crystals. In the liquid-nitrogen irradiated crystals they only found evidence for point defects and very small aggregates. The different size aggregates produced in KCl crystals irradiated at liquid-nitrogen and room temperature were also found by Sonder and Walton.¹⁰

Exact calculations for the scattering of phonons by aggregates in an elastic medium are formidable. The details of the calculations depend on the shape and size of the aggregate as well as the elastic properties of the host medium and the aggregate. However, at the two extremes of phonon frequency the calculations can and have been done exactly.

In the low-frequency limit, where the phonon wavelength is much larger than the diameter of the aggregate ($qa \ll 1$, where q is the phonon wave vector and a is the diameter of the aggregate), several calculations have been done by Trueell and co-workers¹¹⁻¹³ and Pao and Mow.¹⁴ They calculated the scattering of longitudinal and shear waves in an isotropic elastic solid by an isotropic elastic sphere, a spherical cavity, a rigid sphere, and a fluid filled cavity. In all cases the total scattering cross section σ varies as

$$\sigma_{\text{long wavelength}} \propto \omega^4,$$

which is the classical Rayleigh scattering law. For a thin platelet of atoms of different mass and atomic volume, Turk and Klemens¹⁵ calculated the total scattering cross section also to be proportional to ω^4 in the long-wavelength limit.

In the high-frequency limit, i.e., $qa \gg 1$ the problem is one in geometrical optics. A spherical aggregate presents a constant cross section to all incoming phonons independent of incident direction and its scattering cross section is independent of phonon frequency. If the aggregate is not spherical then its effective size depends on the direction of the incident phonon. But the cross section must again be frequency independent and must depend on some average of the size of the aggregate. To find the phonon scattering by a platelet in the short-wavelength limit, Turk and Klemens¹⁵ considered near-normal incidence of phonons onto thin impurity platelets with diameters large compared to the phonon wavelength. They found the scattering cross section to be proportional to ω^2 and thus not independent of frequency as with a spherical aggregate. However, Schwartz and Walker, who had disk-shaped precipitates of diameter 100 Å and thickness 15 Å, fitted their results quite well with a relaxation rate that was frequency independent in the high-frequency limit. This would seem to indicate that thicker platelets scatter phonons with a cross section that is frequency independent in this limit. The problem then arises how thin or thick a platelet must be for the scattering cross section to be proportional to ω^2 or to be independent of frequency. The calculations would seem to be formidable.

For phonon frequencies in the range $qa \approx 1$, the transition or changeover region from geometrical to Rayleigh scattering, no analytic expressions exist but there are numerical calculations which enable one to estimate the scattering behavior. Both Anderson¹⁶ and Walton and Lee¹⁷ agree that there are three types of behavior expected in the transition region: oscillatory, single peak, or a smooth Rayleigh to geometrical transition depending upon the properties of the sphere (aggregate) and the matrix. However, Schwartz and Walker did some numerical calculations and found that the thermal conductivity does not oscillate in the transition region even though the cross section does. Their results and those of Walton all appear to be smooth transitions from Rayleigh to geometrical scattering.

II. EXPERIMENTAL

The experimental procedure has been described elsewhere.^{18,19} The four diamonds (IIa-1, IIa-3, IIa-4 and IIa-5) were type IIa according to their uv transparency limit. Type-IIa diamonds contain

considerably less nitrogen and are purer than type-I diamonds.

The original dimensions of the diamonds were $\Pi a-1$: $10.6 \times 1.09 \times 1.09 \text{ mm}^3$; $\Pi a-3$: $10.0 \times 1.27 \times 1.30 \text{ mm}^3$; $\Pi a-4$: $10.5 \times 1.290 \times 1.295 \text{ mm}^3$; and $\Pi a-5$: $9.3 \times 1.295 \times 1.315 \text{ mm}^3$. The diamonds were polished with 4–8- μm diamond grit. To produce an opaque rough-surface diamond, $\Pi a-1$ was annealed at 1100 °C for 10 h in an argon atmosphere (runs 47 and 54). For run 56 this layer was polished off. For run 88 on $\Pi a-1$, run 83 on $\Pi a-4$, runs 84 and 96 on $\Pi a-5$, and runs 91 and 95 on $\Pi a-3$, the diamonds were annealed at temperatures from 1100 to 1350 °C for 10 h in a bakable ultrahigh-vacuum system with vacion and titanium sublimation pumps giving a vacuum of between 10^{-7} and 10^{-9} Torr (a high-vacuum anneal). Optical microscope pictures with a magnification of 500 \times showed that the polish marks had not been affected by the high-vacuum anneal. However, the phonon scattering off polished and off high vacuum annealed polished surfaces is not the same suggesting that a change took place just underneath the surface.^{18,20}

The diamonds were irradiated with 0.75-MeV electrons and a current density of 2 $\mu\text{A cm}^{-2}$. For the first irradiation of $\Pi a-1$ the current density was only very approximately 2 $\mu\text{A cm}^{-2}$ and was very probably less. Because the penetration depth (about 0.78 mm) is about half to three-quarters of the thickness, the diamonds were irradiated on each of two opposite sides for the same time. Since the electron energy is just not high enough to produce a significant number of multiple defects, the large majority of defects will be isolated Frenkel pairs (assuming a displacement energy of 80 eV). Any evidence for irradiation produced aggregates will thus require interstitial mobility.

Diamonds $\Pi a-1$, $\Pi a-4$, and $\Pi a-5$ were irradiated at room temperature, while $\Pi a-3$ was irradiated at 77 K.

III. THEORY

At low temperatures, where the phonon density of states is very well approximated by the Debye density and where normal processes can be neglected,²¹ the Debye theory is well suited to describe the thermal conductivity. This theory leads to the equation (called the Debye model for thermal conductivity²²)

$$K = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta/T} \tau(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

where $x = \hbar\omega/k_B T$, v is an appropriately averaged sound velocity (the Debye velocity here), and $\tau(x, T)$ is the total phonon relaxation time and the other symbols have their usual meanings. When

more than one scattering mechanism is present the usual combined relaxation-time assumption, based on the lack of evidence for interdependence of scattering mechanisms, gives

$$\tau^{-1}(x, T) = \sum_i \tau_i^{-1}(x, T), \quad (2)$$

where τ_i is the relaxation time for the i th scattering mechanism.

At low temperatures only the intrinsic boundary, isotope, impurity point-defect and dislocation scattering, and the irradiation produced point-defect and/or aggregate scattering need be considered. The total inverse relaxation time can then be written in terms of ω and T as

$$\tau^{-1}(\omega, T) = v \left(\frac{1}{L_C} \frac{1 - P(\omega)}{1 + P(\omega)} + \frac{1}{L} \right) + A\omega^4 + D\omega + \tau_{\text{aggregate}}^{-1}, \quad (3)$$

where L_C is the Casimir length ($L_C = 1.12d$ where d is the width of the diamond), L is the length of the diamond, and $P(\omega)$ depends on the phonon frequency ω and the surface roughness. The first term, which is the boundary scattering term, takes specular reflection and the length correction into account.^{23,24} The second term represents both scattering by isotopes and impurity point defects present in the unirradiated crystal and scattering due to irradiation produced point defects. The parameter A is thus a measure of the point-defect concentration. $D\omega$ represents dislocation scattering, which, however, could be neglected because it was found to be very small.

If the irradiation-produced aggregates are approximately spherical in shape, the aggregate scattering relaxation rate can be written²

$$\begin{aligned} \tau_{\text{aggregate}}^{-1} &= C\omega^4 \quad \text{for } qa < 1, \\ \tau_{\text{aggregate}}^{-1} &= Nv\pi a^2/4 \quad \text{for } qa \geq 1, \end{aligned} \quad (4)$$

where a is the effective diameter, N is the concentration of the aggregates, q is the phonon wave vector, and

$$C = N\pi a^6/4v^3.$$

This equation corresponds to a constant scattering cross section for $qa \geq 1$ and a Rayleigh scattering cross section for $qa < 1$. The aggregate size is determined from the temperature at which the scattering changes from geometrical to Rayleigh. However, this changeover depends on the particular theoretical model used and even then is still not well defined. For this reason it was decided that in the model used here [Eq. (1) to (4)], which is a simple one since no differences in density and elastic constants between the aggregates and the lattice have been considered,

the changeover condition should be chosen between $qa=1$ and $qa=1.5$ to give a range of aggregate sizes rather than just one value. The condition that the changeover occurs at the temperature at which $qa=1$ (where $\lambda=2\pi a$) rather than at the temperature where $\lambda \approx a$ is commonly used and comes from the work of e.g. Rayleigh²⁵ and Truell and Ying.¹¹ Apparently, Rayleigh's theory applies to particles that are no longer than about $\frac{1}{10}$ of the wavelength.²⁶

Equation (1) with the total relaxation time given by Eq. (3) and (4) was used to fit the experimental results.

IV. EXPERIMENTAL RESULTS

In Figs. 1–5 the experimental results are given by the points and the solid lines are the computer fits. The parameters that gave the best fits are summarized in Table I.

The experimental results are given as plots of K/T^3 vs T to clearly show the change from geometrical scattering ($K/T^3 = \text{constant}$) to Rayleigh scattering (sharply increasing value of K/T^3). Also, since simple boundary scattering by rough surfaces gives a constant K/T^3 value²⁷ (called the corrected theoretical Casimir value), the resulting K/T^3 value (due to boundary, aggregate and impurity point-defect scattering) will lie below this Casimir value in the short wavelength limit but go above it in the long-wavelength limit. For these reasons it is believed that K/T^3 -vs- T plots are more informative than a plot of $\log_{10}K$ vs $\log_{10}T$.

Ideally, the same surface conditions should have been used for all irradiated diamonds. However, at the time of these experiments boundary scat-

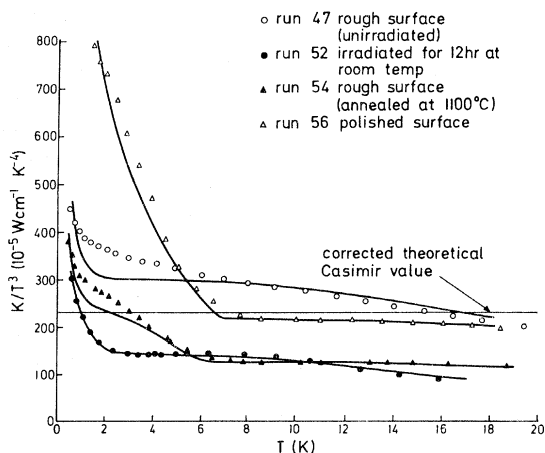


FIG. 1. Plot of K/T^3 vs T for diamond IIa-1; (1) before and (2) after a room-temperature irradiation, (3) after an anneal at 1100 °C, and (4) after polishing of the rough surface.

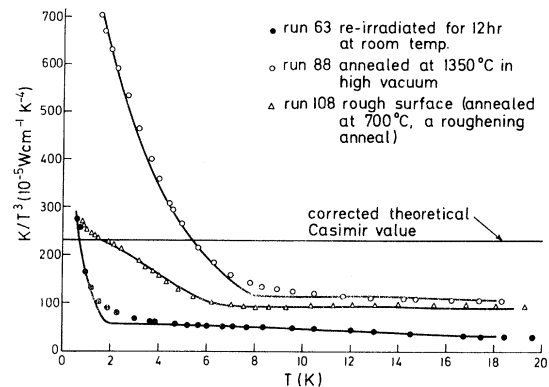


FIG. 2. Plot of K/T^3 vs T for diamond IIa-1; (1) after reirradiation, (2) after an anneal at 1350 °C, and (3) after roughening of the surface.

tering by rough, polished and high-vacuum-annealed polished surfaces and the nearly frequency-independent scattering with a phonon mean free path over twice the Casimir value in polished diamonds were still being investigated.¹⁸⁻²⁰ These three surface finishes were found to scatter phonons differently and thus gave rise to different values for the parameters $P(\omega)$ and the phonon mean free path. However, the parameters a (diameter) and N (concentration) would be expected to remain the same when changing the surface condition. This was checked on diamond IIa-1 and the results can be seen in Table I (from run 54 to 56 and from run 88 to 108). The diameter a remained approximately constant while N seems to have been affected. But these changes in N can be explained as being due to experimental form factor errors (up to about 8%) and errors in the value of $(1/L_c)[1+P(\omega)]/[1-P(\omega)]$ (up to about 15%) used.

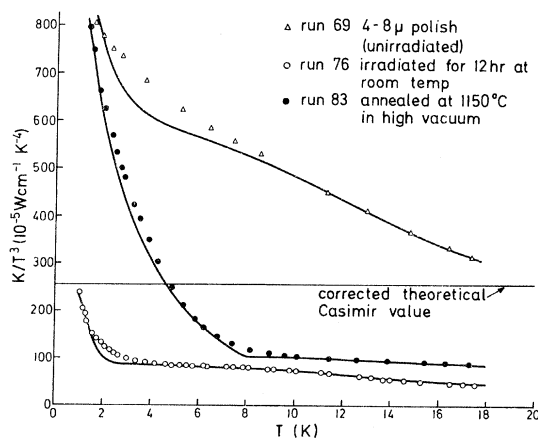


FIG. 3. Plot of K/T^3 vs T for diamond IIa-4 before and after a room-temperature irradiation and after a subsequent anneal at 1150 °C.

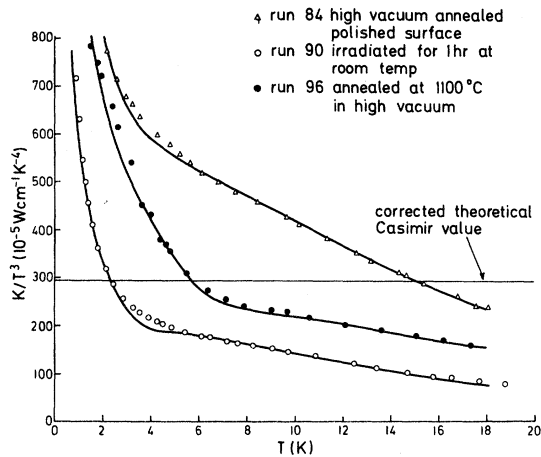


FIG. 4. Plot of K/T^3 vs T for diamond IIa-5 before and after a room-temperature irradiation and after a subsequent anneal at 1100 °C.

The following observations regarding the experimental results and the fits are worth noting: A 12-h room-temperature electron irradiation of diamonds IIa-1 (run 52 in Fig. 1) and IIa-4 (run 76 in Fig. 3) and a 1-h irradiation of IIa-5 (run 90 in Fig. 4) resulted in curves that are characteristic of phonon scattering by aggregates (113–170, 120–180, and 67–100 Å, respectively). K/T^3 changes from a constant or nearly constant value (geometrical scattering) to a rapidly increasing one at lower temperatures (Rayleigh scattering). These curves can definitely not be fitted with only a point-defect scattering term in the high-frequency-limit range.

Approximately the same dose of irradiation produced nearly the same size aggregates (113–170 and 120–180 Å in IIa-1 and IIa-4, respective-

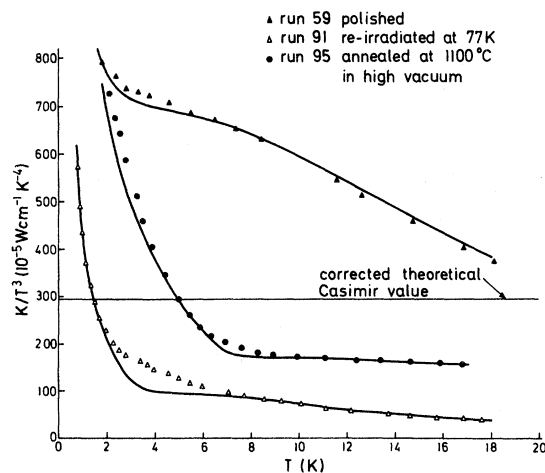


FIG. 5. Plot of K/T^3 vs T for diamond IIa-3 before and after an irradiation at 77 K and after a subsequent anneal at 1100 °C.

ly), while a smaller dose produced smaller aggregates (67–100 Å in IIa-5).

The parameter A , which is a measure of the point defect concentration including the irradiation produced vacancies and interstitials, was found to be larger for all the irradiated diamonds than for the unirradiated ones. This explains why at higher temperatures, K/T^3 for the irradiated diamonds is not constant but decreases with increasing temperature since that is the temperature region where point-defect scattering becomes important ($\tau_{pd}^{-1} \propto \omega^4$). For all runs on IIa-5 (both unirradiated and irradiated) the decrease in K/T^3 with increasing temperature is more pronounced than for the other diamonds. This agrees with the value of A for the unirradiated IIa-5 ($A = 7.8 \times 10^{-46} \text{ sec}^3$) being larger than that found for the other unirradiated diamonds. IIa-5 is thus the “least pure” of the four studied. The purest of the four diamonds IIa-1 ($A = 1.53 \times 10^{-46} \text{ sec}^3$) does show a nearly constant K/T^3 value between 2 and about 9 K (run 52, Fig. 1) while above this temperature the small amount of point-defect scattering becomes important.

Annealing the irradiated IIa-1, IIa-4, and IIa-5 at 1100 °C or slightly higher for 10 h resulted in the K/T^3 value turning up sharply below about 7–8 K in all cases [runs 54 and 88 for IIa-1 (Fig. 1 and 2), run 83 for IIa-4 (Fig. 3), and run 96 for IIa-5 (Fig. 4)]. The size of the aggregates was determined to be about 37–55 Å with a concentration greater than that for the larger aggregates. Also, for all three diamonds the parameter A was found to be smaller than that for the unirradiated diamond. For this reason K/T^3 for runs 54, 56, 88, and 108 on IIa-1 is approximately constant even at higher temperatures.

Reirradiation of IIa-1 for 12 h resulted in the 37–55-Å aggregates growing in size to 146–220 Å (run 63, Fig. 2), while the concentration of the aggregates appears to have decreased even taking into account the experimental form factor errors and errors in the boundary scattering term. The observed decrease in N (from run 56 to 63), while a constant value or increased value was expected can be due to the fact that since the diamond had a polished surface with, as was mentioned earlier, the resulting unusual phonon scattering,^{18–20} the parameters in the boundary scattering term introduced a larger error than originally estimated. Also only one value of the aggregate diameter a was used in the computer fits while naturally a whole range of aggregate sizes would be expected. The use of only one size aggregate in the computer fits explains why the experimental points and the theoretical fits do not agree very well in the changeover region for the curves of the diamonds

TABLE I. Summary of parameters that best fitted the runs on diamonds IIa-1, IIa-3, IIa-4, and IIa-5. IIa-1, IIa-4, and IIa-5 were irradiated at room temperature while IIa-3 was irradiated at 77 K.

Diamond	Run No.	Treatment	Surface	$A(10^{-46} \text{ sec}^3)$	a (Å)	$N(10^{12} \text{ cm}^{-3})$
IIa-1	47	Unirradiated	rough	1.53	0	
	52	Irradiated (12 h)	rough	10.0	113-170	6.3- 2.8
	54	Annealed at 1100 °C	rough	0.68	37-55	83.3-37.0
	56	Same as run 54	polished	0.34	37-55	63.0-28.0
	63	Reirradiated (12 h)	polished	27.0	146-220	20.5- 9.1
	88	Annealed at 1350 °C	H.V. annealed ^a	0.68	36-54	150.8-67.0
	108	Annealed at 700 °C	rough	0.68	38-57	130.5-58.0
IIa-4	69	Unirradiated	polished	4.4	0	0
	76	Irradiated (12 h)	polished	20.0	120-180	18.7- 8.3
	83	Annealed at 1150 °C	H.V. annealed	2.7	37-55	166.5-74.0
IIa-5	84	Unirradiated	H.V. annealed	7.8	0	0
	90	Irradiated (1 h)	H.V. annealed	31.0	67-100	15.8- 7.0
	96	Annealed at 1100 °C	H.V. annealed	5.1	37-55	49.5-22.0
IIa-3	59	Unirradiated	polished	2.7	0	0
	74 & 79	Irradiated (16 min) and then annealed at 1100 °C	H.V. annealed	5.1	0	0
	91	Reirradiated (48 min)	H.V. annealed	68.0	80-120	31.5-14.0
	95	Annealed at 1100 °C	H.V. annealed	1.0	37-55	83.3-37.0

^a H.V. stands for high vacuum.

with large aggregates. The good fits of the curves for the 37-55-Å aggregates indicate a very small spread in sizes after the anneals at 1100 °C.

Diamond IIa-3 was irradiated at 77 K for about 16 min., raised to room temperature and only then cooled down for thermal conductivity measurements (run 74). Next it was annealed at 1100 °C in a high vacuum (run 79). The K/T^3 curves for these two runs were similar in shape to the curve for the run on the unirradiated diamond (run 59) but both were slightly lower with the curve for the irradiated diamond (run 74) below the curve for the annealed case (run 79). There was no evidence for aggregate scattering; just point defect scattering was observed. After the anneal A was found to be $5.1 \times 10^{-46} \text{ sec}^3$ compared to $2.7 \times 10^{-46} \text{ sec}^3$ for the unirradiated diamond indicating that not all the irradiation damage had been annealed out. A 48-min reirradiation of diamond IIa-3 at 77 K and the subsequent warming up to room temperature resulted in 80-120-Å aggregates (with a large spread in sizes) and a very large number of point defects (a large A value, run 91 in Fig. 5). Compared to the 1-h room-temperature irradiation of IIa-5 (run 90) this 77-K irradiation seems to be a more effective producer of defects (both more and larger aggregates and more point defects). As with the other three diamonds an anneal at 1100 °C (run 95, Fig. 5) resulted in 37-55-Å aggregates with a higher concentration than that of the larger ag-

gregates, which were present before the anneal, and a value of A lower than that for the unirradiated diamond.

V. DISCUSSION AND CONCLUSION

The experimental results presented in Sec. IV indicate the formation of aggregates in electron irradiated diamonds. These aggregates must consist of interstitials, since in diamond the vacancy only becomes mobile well above room temperature,⁷ i.e., well above the irradiation temperature. It is now necessary to calculate the approximate number of interstitials produced and to see if it is possible to accommodate them into aggregates, of various shapes and densities, with the concentrations determined from the observations.

The number of displaced carbon atoms per cm^3 as a result of the electron irradiation can be calculated to an order of magnitude by the equation

$$N_d = N_0 \sigma_d n_e,$$

where N_0 is the number of carbon nuclei per cm^3 , σ_d is the total displacement cross section for 0.75-MeV electrons, and n_e is the total number of incident electrons per cm^2 . For a 0.75-MeV electron beam with a current density of $2 \mu\text{A}/\text{cm}^2$ and for a total of 12 h irradiation, N_d is found to be 2.0×10^{17} atoms/ cm^3 . This number includes a 10% correction for the energy loss of the electrons in the crystal.

The total number of atoms needed to form spherical aggregates or platelets of the observed diameters can now be calculated and can then be compared to N_d . The number of carbon atoms, which is the same as the number of interstitial positions, in a sphere of 180-Å diameter is 5.35×10^5 . For run 76 on $\Pi a-4$ the concentration of 180 Å aggregates was found to be 8.3×10^{12} per cm^3 so a total of about 4.5×10^{18} atoms would be needed to fill all interstitial positions. A sphere with a 120-Å diameter (the lower limit of the aggregate size for run 76) and a concentration of 18.7×10^{12} would need the same number of atoms to fill all interstitial positions. However, it is of course extremely unlikely if not physically impossible for all the interstitial positions to be filled. Since only about 2×10^{17} atoms were displaced, the formation of a 180 Å (or 120 Å) spherical aggregate with the above concentrations would only be possible if the increase in density of the aggregate with respect to the diamond lattice was small [(5-10)%]. This seems physically much more likely than a large increase in density.

For a platelet of 180-Å diameter and 5-Å thickness there are about 2.5×10^4 interstitial positions. The number of atoms needed in this case to fill all interstitial positions would be 1.6×10^{17} , which is less than the total knocked out. The formation of a platelet is thus very possible. The 5-Å thickness was arbitrarily chosen. It could have been larger for the numbers still to agree assuming that not all interstitial positions were filled.

Similar calculations of this nature were also done for run 90 on $\Pi a-5$ and for run 52 on $\Pi a-1$ and the same results as above were obtained; that based solely on numerical considerations the formation of spherical aggregates with a small increase in density or platelets with some or all interstitial positions filled is possible.

It is interesting to note that the total number of atoms in the 180-Å aggregates (4.5×10^{18}) is comparable to the concentration of nitrogen atoms since type-IIa diamonds have less than about 5×10^{18} nitrogen atoms per cm^3 and an average concentration on the order of 10-15 ppm (about 10^{18} cm^{-3}).²⁸ But it seems extremely unlikely that all nitrogen atoms will aggregate since only a fraction of them are displaced by the electron irradiation.

If the aggregates are platelets then, based on the calculations of Turk and Kelmens, the scattering relaxation rate would be expected to be proportional to ω^2 in the high-frequency limit. However, the results could definitely not be fitted with a ω^2 term instead of a frequency-independent term in this limit. The aggregates can thus not be very thin platelets, but, as was discussed earlier, thicker

platelets could possibly scatter phonons with a frequency-independent relaxation rate and thus account for the observed conductivity.

The calculation of the number of displaced carbon atoms was based on an displacement energy of 80 eV. However, very recent work²⁹ seems to indicate that this value is too high and that it is more like 60 eV. In that case more defects will have been produced and the formation of spherical aggregates with a larger increase in density (greater than about 10%) or thicker platelets will be possible.

The turnups in the K/T^3 curves after the first irradiation cannot be explained as being due to resonant processes (e.g., localized modes) or due to phonon-electron scattering since different doses resulted in turnups at different temperatures (runs 52 on $\Pi a-1$ and 90 on $\Pi a-5$). The curves would all have turned up at the same temperature if a resonant process or electron scattering were present. The curves for all the diamonds after an irradiation and subsequent anneal at or above 1100 °C did all turn up at about the same temperature (7-8 K) indicating that a resonant process could be responsible. However, the reirradiation of $\Pi a-1$ (run 63) seemed to indicate the growth of the already existing 37-55-Å aggregates. This latter aspect, the formation of small aggregates or resonance centers after an anneal, needs a much more thorough investigation though.

The formation of interstitial aggregates in both the room-temperature and 77-K irradiated diamonds shows that the interstitial in diamond must be mobile at or below room temperature. It is unlikely that it is mobile at 77 K since the diamond irradiated at the temperature had more irradiation produced defects than a diamond irradiated with about the same dose at room temperature. Only if approximately the same number of defects had been produced in these two cases, would it be possible to say that the interstitial is mobile at 77 K. This result, that the interstitial becomes mobile below or at room temperature, is in agreement with the recent suggestion made by Lomer and Wild.⁵

VI. SUMMARY

The low-temperature thermal conductivity of 0.75-MeV electron irradiated type-IIa diamonds was found to be reduced and provides strong evidence for the formation of interstitial aggregates in these diamonds. This conclusion is based on the shape of the K/T^3 -vs- T curve for an irradiated diamond. K/T^3 changes from a nearly constant value (geometrical phonon scattering) to a rapidly increasing value at lower temperatures (Rayleigh scattering). It would be desirable to support this

conclusion with other evidence, such as electron microscope pictures, but that is beyond the purpose and scope of this paper.

Calculations of the number of displaced atoms and the number needed to form aggregates show that sufficient atoms have been displaced to form aggregates. If these aggregates are spherical, then they can only have a small increase in density and if they are thin platelets then some or all interstitial positions can be filled. A combination of the two is also possible.

An anneal at or above 1100 °C of all irradiated diamonds resulted in all the large aggregates being reduced to 37–55 Å. This size aggregate appears to be the permanent irradiation damage in diamond and must thus correspond to some ther-

mally stable configuration in the diamond lattice.

The irradiation of one diamond at 77 K showed that this low-temperature irradiation was a much more effective producer of defects than a similar dose in a room-temperature irradiated diamond. Also since aggregates were formed in the diamond irradiated at 77 K and subsequently annealed to room temperature, the interstitial in diamond must be mobile below or at room temperature.

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