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Boundary scattering in five natural type-II*a* diamonds

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The thermal conductivity in the boundary scattering region of five type-II*a* diamonds with different surface finishes was investigated. With polished surfaces the boundary scattering was found to be nearly temperature independent but with a phonon mean free path two to three times the Casimir value. After a chemical etch or a high-vacuum high-temperature anneal the scattering became temperature dependent, and the conductivity was more in agreement with the height of the surface asperities. It is suggested that in polished diamonds the phonons interact with the strain field associated with the network of microcracks underneath the abraded surface.

I. INTRODUCTION

During the past 20 years the technique of low-temperature thermal conductivity measurements has been used increasingly as a means for studying the interaction between phonons and lattice defects. The thermal conductivity of pure and perfect crystals of dielectric materials at low temperatures does not have a unique value for the material but depends upon the crystal dimensions. Casimir[1] was the first to develop an approximate theoretical explanation of this boundary-limited conductivity by considering the heat flow in a cylindrical, infinitely long, isotropic crystal with perfectly diffuse walls. In this case the conductivity is proportional to the temperature cubed and the diameter.

Berman, Simon, and Ziman[2] and Berman, Foster, and Ziman[3] were the first to confirm this with work on diamonds and sapphires, respectively. They also computed modifications of Casimir's theory for crystals of finite length with various amounts of specular reflection. This yielded a modified size effect, in which the conductivity is no longer simply proportional to the crystal diameter, but is dependent on the ratio of crystal radius to length and on the surface roughness. They showed that not only did specular reflection increase the conductivity by a factor $(1+P)/(1-P)$, where P varies with surface condition but that it was also temperature dependent. The variation with temperature occurs because with decreasing temperature the average phonon wavelength increases and eventually a surface of given roughness appears smoother. Hurst and Frankl[4] confirmed this modified size effect with work on high-purity silicon but found that phonons travelling in a certain direction, $\langle 100\rangle$, are reflected with appreciable specularity even from rough surfaces. This latter observation was explained by McCurdy, Maris, and Elbaum,[5] who described another way in which the conductivity may differ from the predictions of Casimir. They showed the conductivity in the boundary regime to depend on the orientation of the crystal rod axis. That anisotropy was accounted for in terms of phonon focusing due to the fact that in elastically anisotropic cubic crystals the phonon phase and group velocities are, in general, not collinear. They generalized Casimir's theory to include the effects of focusing.

Thacher,[6] working on LiF with rough sandblasted surfaces, found the conductivity to be proportional to the temperature cubed but found the phonon mean free path (the distance between diffuse reflections) to be about 20% larger than that predicted theoretically. Others (e.g., Pohl,[7] Klein,[8] and Harrington and Walker[9]) working on alkali halides also found discrepancies between the experimentally determined mean-free-path and the theoretically predicted value. This difference was usually attributed to the wrong value having been used for the averaged sound velocity and some specular reflection being present. Worlock,[10] however, suggested that it is not surface roughness which is responsible for diffuse scattering but the tangle of dislocation loops produced beneath the surface by the impact of the abrasive particles when roughening a surface. He suggested several experiments to check this hypothesis. Thacher did these and found his results to be consistent with Worlock's suggestion. From his results Thacher concluded that some unknown mechanism must be responsible for the frequency-independent specular reflection off the dislocation network present underneath a rough sandblasted surface.

In the present study boundary scattering experiments were conducted on five natural type-II*a* diamonds with different surface finishes. Optical and electron microscope pictures were taken of the surfaces and the size of the surface asperities measured. Because of its very high Debye temperature (about 2200 K), diamond has its thermal conductivity peak at a relatively high temperature (70–80 K) and thus has a large region where boundary scattering predominates. This region can be up to at least 10 K for very pure diamonds and is thus larger than for alkali halides, in which boundary scattering dominates up to only about 5 K. For the same reason diamond has the advantage that the wavelength of the dominant phonons at low temperatures is longer than for any other crystals, so a good comparison of these with the surface asperities is possible.

II. EXPERIMENTAL

The apparatus used for measuring the thermal conductivity was a conventional ^{3}He cryostat, similar to the one reported by Walton,[11] and capable of operation to 0.3 K. The diamond holder was similar to a design used by Berman, Simon, and Ziman. The heater was pressed by means of a screw onto the bottom end of the diamond. The top end was pressed into the base of a small copper rod which was connected to the bottom of the ^{3}He bath. The heat thus entered the diamond at the bottom and exited at the top. The two thermometers were germanium resistors with a range of resistances from about 20 Ω at 20 K to 40 000 Ω at 0.3 K thus giving a very high sensitivity. These thermometers were calibrated against two other germanium resistors which were calibrated against primary temperature standards. The absolute readings of the thermometers can thus be expected to have a very slight error but the relative readings should not be affected. Thermal contact of the thermometers to the diamond was made with indium coated clamps tightened by small screws. Self-heating of the thermometers was avoided by using appropriate currents and adequate thermal isolation of the thermometers from their surroundings was assured by using the appropriate sized leads. A "two-heater"[12] method was used to correct for any heat lost from the diamond by any other path and to correct for any relative drift in the calibration of the thermometers. With thermometers of the above sensitivity, ΔT, the temperature difference, can be determined to an accuracy of at least 2% below 10 K and to about 4% above this temperature. Measurement of the geometrical factor, the distance between the midpoints of the thermometer clamps, had an accuracy of about 4%. From these considerations it follows that the thermal conductivity measurements have an absolute error of about 7% below and 9% above 10 K. A detailed experimental discussion including test experiments has been given elsewhere.[13]

The five diamonds were type IIa according to their uv transparency limit. The classification of diamonds into types Ia, Ib, IIa, and IIb is given by Berman.[14] Type-II diamonds are much purer and contain considerably less nitrogen than type-I diamonds. The uv absorption curve between 15 000 and the edge at about 45 000 wave numbers (or 5.4 eV) has been called the uv tail. This curve was featureless and only the height of the tail differed for different diamonds. The height of this tail is believed to be an indication of the purity of the diamond[15] (the lower the tail the purer the diamond, see Table II). The diamonds were polished into long rectangular rods of square cross section with typical dimensions of 10×1.3×1.3 mm. They were always polished in such a way that the end faces were dodecahedron faces $\{110\}$ and the side faces dodecahedron and cube faces $\{100\}$. This means that the heat flow was always in or nearly in a $\langle 110\rangle$ direction. These directions were not chosen but resulted because of polishing considerations, i.e., easy polishing directions. For diamonds IIa-1 and IIa-5 the heat flow was exactly in a $\langle 110\rangle$ direction and for diamonds IIa-2 and IIa-7 it was only a few degrees off a $\langle 110\rangle$ direction. For IIa-6 the orientations were not determined since the diamond was destroyed accidentally before this could be done. Calculations by McCurdy *et al.* show that for this orientation in diamond no phonon focusing occurs; the theoretical mean free path they calculated for diffuse scattering being $1.11d$ compared to the expected $1.12d$. No phonon focusing corrections need thus be made. The actual dimensions of each diamond when they were first used were IIa-1, 10.6×1.09 ×1.09 mm; IIa-2, 10.0×1.30×1.25 mm; IIa-5, 9.3×1.295×1.315 mm; IIa-6, 13.1×1.31×1.28 mm; and IIa-7, 11.6×1.33×1.35 mm. Every polish reduced the sides by approximately 0.03 mm. The diamonds were polished with diamond grit of four sizes: $0-\frac{1}{2}$-μm grit, 4–8-μm grit, 50-μm grit, and 30–60-μm grit. All polished surfaces were completely covered with polish marks consisting of ridges and grooves of various sizes. The polish marks on a particular side were in the same direction, at either about 45° or 90° to the long side of the diamond, depending on the easy polishing direction of the side. The polish marks along the length of the diamond on two sides were found only for diamond IIa-6. IIa-1 was annealed at 1100 °C for 10 h in an argon atmosphere and came out cloudy (a surface effect) (run 47). IIa-2 (run 62) was annealed at 1100 °C for 10 h in a poor vacuum and came out black. The surface which had graphitized was cleaned in an acid solution. The above two anneals in which the polish marks had been removed by the thermal etch and the remaining surface was rough and pitted will be called a roughening anneal. Diamonds IIa-2 (run 75), IIa-5 (run 84), IIa-6 (run 107), and IIa-7 (run 113) were annealed at temperatures from 1100 to 1350 °C for 10 h in a bakeable ultrahigh vacuum system with vacion and titanium sublimation pumps giving a vacuum of between 10^{-7} and 10^{-9} Torr (a high vacuum anneal). Both before and after the anneal the diamonds were clear with the polish marks visible to the eye. Optical microscope pictures with magnifications up to 500 taken before and after the anneal showed that nothing had changed on this scale.

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,[6,16] the Debye theory is well suited to describe the thermal conductivity. This leads to the equation (called the Debye model for thermal conductivity)[16]

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

in which v is an appropriately averaged sound velocity; $\tau(x,T)$ is the total relaxation time for the different scattering mechanisms; $x=\hbar\omega/k_BT$; and k_B, $\hbar$, and ω have their usual meaning. When more than one scattering mechanism is present the usual combined relaxation time, based on the lack of evidence for interdependence of scattering mechanisms, is

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

where τ_i is the relaxation time for the ith scattering mechanism. Since normal phonon-phonon scattering processes are neglected in the Debye model, only boundary, isotope, point defect, and dislocation scattering need be considered. The total inverse relaxation time can then be written in terms of ω and T as

$$\tau^{-1}(\omega,T)=v/L_C+B\omega^4+D\omega, \qquad (3)$$

where L_C, called the Casimir length, is the mean free path of the phonons (i.e., the distance between diffuse reflections) for perfectly diffuse boundary scattering. It is equal to the diameter if the crystal is a cylinder or equal to $1.12d$ if the cross section is a square of side d. The first term is the relaxation rate for boundary scattering. $B\omega^4$ and $D\omega$ represent scattering by isotopes and impurity point defects and by dislocations, respectively. The parameter B is thus a measure of the point defect concentration.

At the very lowest temperatures, where boundary scattering is the dominant phonon scattering mechanism, the thermal conductivity is obtained from Eqs. (1) and (3) by considering only the boundary scattering term (i.e., taking $\tau^{-1}=v/L_C$). With the Debye velocity $v=1.32\times10^6$ cm sec^{-1} the following expression, which is similar to that given by Casimir, is obtained:

$$K=2.34\times10^{-2}L_C T^3\ \mathrm{W\,K^{-1}\,cm^{-1}}. \qquad (4)$$

The mean phonon velocity can be calculated in other ways (e.g., taking $\langle v^{-2}\rangle/\langle v^{-3}\rangle$). This has the effect of changing the proportionality constant in Eq. (4) by only a few percent. For example, the ratio of the averages of the inverse square and the inverse cube of the phonon phase velocity for diamond is 1.308×10^6 cm sec^{-1} (using the elastic constants C_{11}, C_{12}, and C_{44} given by McSkiman and Bond[17]) and when substituted into Eqs. (1) and (3) results in the proportionality constant 2.37×10^{-2}.

Equation (4) has to be corrected to take into account the finite length of the diamond.[2] This length correction is of the order of d/L (where L is the length of the diamond) and lowers the theoretical K/T^3 value for perfectly diffuse boundary scattering for diamond IIa-1 by about 10% and for diamond IIa-2 by about 12% (indicated as the corrected theoretical Casimir value in the graphs).

From Eq. (4) it can be seen that K/T^3 is a measure of the phonon mean free path and should be a constant for perfectly diffuse boundary scattering.

However, when the roughness of the surface, given by the height of the surface asperities, is of the order of or less than the wavelength of the dominant phonons (those phonons at temperature T for which $\hbar\omega=3.8k_BT$ since the maximum of the specific heat integral occurs at[18] $x=\hbar\omega/k_BT=3.8$), some of the phonons will be specularly reflected. This causes the temperature dependence of the conductivity to be less than T^3. The phonon mean free path has now become temperature dependent and greater than L_C meaning that K/T^3 is no longer constant but increases with decreasing temperature since the fraction of specular reflections increases with decreasing temperatures.[2,3] This increase in specular reflections is in agreement with the qualitative idea that the surface appears to be smoother the longer the phonon wavelength.

In the purest diamonds point defect impurity scattering becomes noticeable above about 10 K and increases with temperature since its relaxation rate is proportional to ω^4. In this case the phonon mean free path is smaller than L_C and therefore K/T^3 is less than the theoretical Casimir value and decreases with increasing temperature. In less pure diamonds point defect impurity scattering can become important at lower temperatures.

TABLE I. Summary of results on diamonds IIa-1 and IIa-2. The slope ($d \log_{10} K/d \log_{10} T$) was found between 1 and 10 K.

Run	Diamond	Treatment	$d \log_{10} K/d \log_{10} T$
39	IIa-1	50-μm polish	2.91 ± 0.005
40	IIa-1	0–$\frac{1}{2}$-μm polish	2.93 ± 0.005
47	IIa-1	annealed in argon (rough surface)	2.85 ± 0.005
53	IIa-2	50-μm polish	2.87 ± 0.005
57	IIa-2	0–$\frac{1}{2}$-μm polish	2.85 ± 0.005
60	IIa-2	KNO_3 polish	2.54 ± 0.015
62	IIa-2	annealed in poor vacuum (rough surface)	2.82 ± 0.005
73	IIa-2	50-μm polish	2.89 ± 0.005
75	IIa-2	vacuum annealed	2.50 ± 0.015

The experimental results that follow in Sec. IV are given as plots of K/T^3 vs T to clearly show any deviation from the behavior predicted by Casimir for diffuse boundary scattering. For the experimental results reported here this is more informative than a plot of $\log_{10}K$ vs $\log_{10}T$.

The results reported here have actually been fitted with a model consisting of Eqs. (1)–(3) and a term taking specular reflection into account.[13] However, the parameters obtained from the computer fits did not give more useful information about phonon scattering in the boundary region than that already presented here.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The results of all experiments on the two diamonds IIa-1 and IIa-2 are summarized in Table I. The slope of the curves of $\log_{10}K$ vs $\log_{10}T$ was found with a least-squares fit between 1 and 10 K, which is the approximate range of the boundary scattering region. For perfectly diffuse boundary scattering the slope should be 3.00.

A plot of K/T^3 vs T for IIa-1 with three different surface finishes is given in Fig. 1. Curve C (run 47) represents the diamond after a roughening anneal. Pictures of the surface were taken in the electron microscope. The surface consisted of many small pits of an average size of about 300 Å and a smaller number of larger pits with an average size of about 1000 Å. The surface was very nonuniform with steps, pits, and slopes. There were also regions with very little structure or hardly any pits at all. The wavelength of the dominant phonons varies between about 160 Å at 10 K and 800 Å at 2 K. From a comparison of the dimensions of the pits and the phonon wavelengths, curve C would be expected to agree with the corrected theoretical Casimir value except at the lowest temperatures. However, because of the onset of impurity scattering at higher temperatures, curve C falls below the Casimir value. At lower temperatures curve C goes above the Casimir value because of some specular reflection (the phonon wavelengths start to become larger than the surface asperities, especially in those regions where there is very little structure or pits). The specular reflection becomes pronounced below about 2 K because the dominant phonon wavelength increases sharply at these very low temperatures (from about 800 Å at 2 K to 1600 Å at 1 K and to 3200 Å at 0.5 K).

Curves A (run 40) and B (run 39) represent a 0–$\frac{1}{2}$-μm and a 50-μm diamond grit polish, respectively. Very surprisingly the curves are nearly identical. Both have a very slight temperature dependence between 1 and 10 K, the conductivity being proportional to $T^{2.9}$, and have a phonon mean free path about three times the Casimir value in this range. Observations with a phase contrast optical microscope of the 50-μm polished surfaces

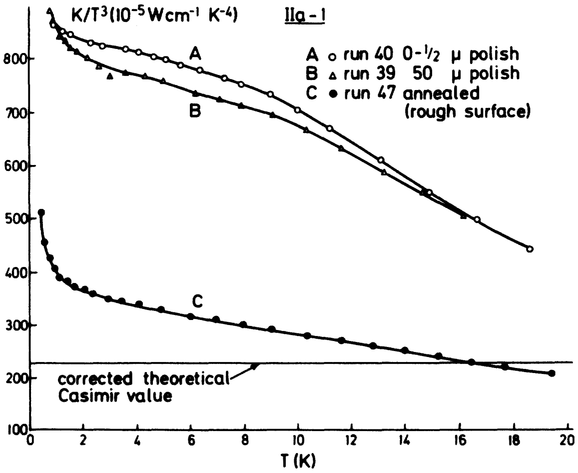

FIG. 1. Plot of K/T^3 vs T for three different surface finishes on diamond IIa-1.

showed scratches with a width of 3–10 μm. From the width of the shadows the depth was determined to be up to about 3 μm. The scratches of the $0-\frac{1}{2}$-μm polished surface were barely visible at magnifications of up to 500. The use of an electron microscope and a carbon-platinum replica technique gave some additional information. The 50-μm polish showed many small ridges and grooves inside and between the main polish marks. These smaller scratch marks had a width of between 300 and 1500 Å and a depth of between 100 and 600 Å. The lower limits of these dimensions were based on the maximum magnification of 15 000 times which was used. Driver[19] has shown that more and more scratches become visible inside and between the smaller grooves at higher magnifications. The smallest asperities he found were about 50 Å in size. He believes it is very difficult to determine the exact depth of the scratches because of the presence of so many scratches inside each other and the difficulty of exactly defining the edges of the scratches. The $0-\frac{1}{2}$-μm polish had ridges and grooves of about the same sizes as the smaller scratch marks on the 50-μm polished surface.

From a comparison of the dimensions of the scratches and the phonon wavelengths, specular reflection would have been expected to dominate at the lowest temperatures and diffuse scattering at the highest temperatures of the boundary scattering region. A nearly temperature-independent scattering between 1 and 10 K with a phonon mean free path of about three times the Casimir value was certainly not expected. These results thus show that in this temperature region the phonons cannot be scattered by the surface asperities (ridges and grooves) but must be scattered before reaching the surface. This scattering process is nearly temperature independent since the conductivity of the polished diamond is very nearly proportional to T^3 (slopes of 2.91 and 2.93 instead of 3.00). Also, since the phonon mean free path is about three times the Casimir value it follows that this scattering process is specular. Hence, it is a nearly-frequency-independent specular scattering process. But at very long wavelengths (below about 1 K for IIa-1 and 2 K for IIa-2) frequency-dependent specular reflection clearly dominates. In no way can defect and dislocation scattering in the bulk of the diamond explain these results because it would make the mean free path smaller than the Casimir length, not larger. Defect and dislocation scattering are the reason for the increase in the temperature dependence (i.e., faster decrease) of K/T^3 above about 10 K. Since all natural diamonds contain about 1% of the ^{13}C isotope, it would be interesting to see if this isotope or the impurity point defects are the cause of the slope being less than 3.00. Using the isotope effect relaxation rate given by Klemens,[20] the value of B [in Eq. (3)] for the ^{13}C isotope is found to be 0.14×10^{-46} sec^3. From Eqs. (1) and (3), with only the boundary scattering and isotope relaxation rates, values of K can be determined which can then be used to find the slope between 1 and 10 K. The slope was found to be 2.996 thus indicating that it is the scattering by the impurity point defects and not by the isotopes that results in slopes with values of about 2.90.

Results on diamond IIa-2 are shown in Fig. 2 and agree very well with the results on IIa-1. Curve D (run 62) represents the annealed, roughened surface which was completely covered with a very large number of small pits up to 600 Å in size and a few larger regions up to several thousand Å of what appears to be hardly affected original surface. The small pits were very closely spaced to each other. As with diamond IIa-1, from the dimensions of the pits and the nonuniformity of the surface, curve D would be expected to agree with the corrected theoretical Casimir value but falls below it because of impurity scattering at high temperatures and increases above it because of specular reflection at low temperatures.

Curves A (run 57) and B (run 53) represent the $0-\frac{1}{2}$- and 50-μm polish, respectively. The fact that these curves do not agree as well as the corresponding curves in Fig. 1 is most likely due to form factor errors of about 4%. These curves show a slight temperature dependence, the conductivity being proportional to $T^{2.87}$, and a phonon mean free path between two and three times the Casimir value in the boundary scattering region. The important point is that the conductivity for each diamond with polished surfaces has a temper-

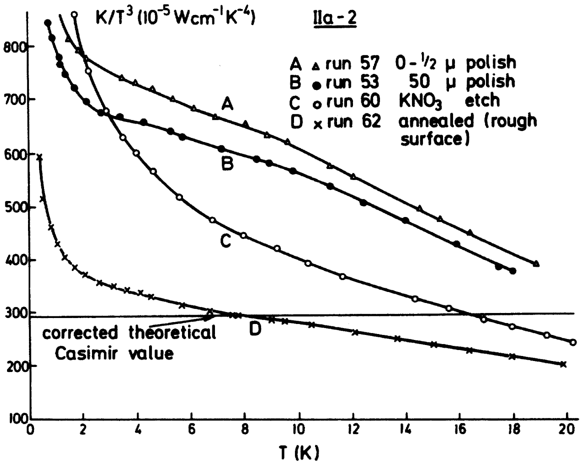

FIG. 2. Plot of K/T^3 vs T for four different surface finishes and treatments on diamond IIa-2.

ature dependence nearer to T^3 (slopes from 2.85 to 2.93) than that for the diamonds with roughened annealed surfaces (slopes from 2.82 to 2.85). The significance of this is that it shows that the scattering process below the polished surface is nearer to perfectly diffuse boundary scattering than the actual scattering off the rough surfaces even though the phonon mean free path is two to three times the Casimir length. These slopes for the roughened surfaces seem very reasonable when compared to the values found by Hurst and Frankl[4] who, in their work with rough-surfaced high-purity silicon crystals, determined the slopes to be between 2.90 and 3.00. For rough-surfaced high-purity germanium crystals, Frankl and Campisi[21] found the slope to be "well below 3.00" and attributed it to isotope and impurity scattering. To get an exact T^3 dependence very high-purity samples would be needed. To investigate the baffling nearly frequency independent scattering with a phonon mean free path over twice the Casimir value the following two experiments were done on II*a*-2.

Curve *C* (run 60) represents a potassium nitrate etch at 600 °C for 3 h. Electron microscope pictures showed that the etch had attacked the polish ridges, smoothing them slightly and had left quite a few small etch pits on the surface. The polish marks are still clearly visible but a considerable number of etch pits, up to about 700 Å in size and spaced from about 500 Å to thousands of Å apart, now cover the surface. From a comparison of the dimensions of the ridges, grooves and pits with the phonon wavelengths, some specular reflection would be expected at the lowest temperatures and diffuse reflection at higher temperatures. Curve *C* shows this with a temperature dependence of $T^{2.54}$ and a phonon mean free path rapidly increasing with decreasing temperature. This indicates that the phonons are reflected off the surface itself.

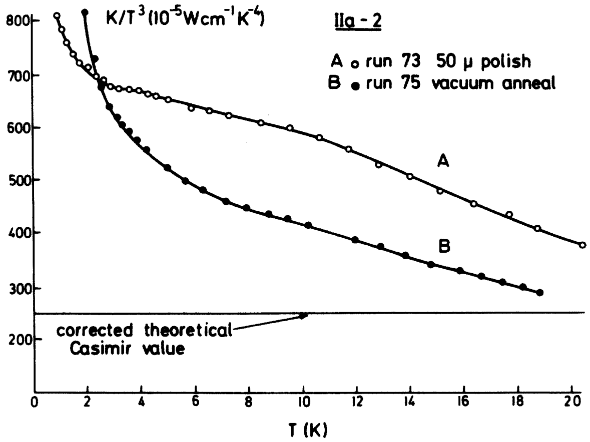

FIG. 3. Plot of K/T^3 vs T for diamond II*a*-2 with a 50-μm polished surface (curve *A*) and after a high vacuum anneal (curve *B*).

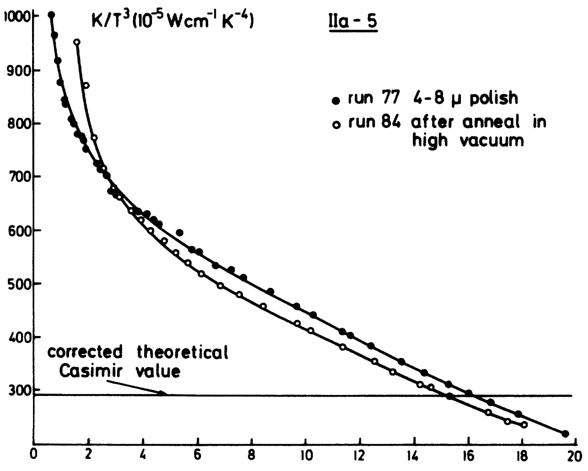

FIG. 4. Plot of K/T^3 vs T for runs on diamond II*a*-5 with a 4–8-μm polished surface and after a high vacuum anneal.

Curve *B* (run 75 in Fig. 3) shows the effect of a high vacuum anneal of II*a*-2 with a 50-μm polished surface. As in the case of the chemically etched surface, the high-vacuum-annealed diamond gave a conductivity, which was proportional to $T^{2.50}$, more in agreement with the surface finish than that of the 0–$\frac{1}{2}$- and 50-μm polished diamonds. Especially for the "rougher" 50-μm polished surface diffuse scattering would have been expected at higher temperatures.

The high-vacuum-annealing result (run 75) was surprising because no noticeable change in the surface structure had taken place. This annealing experiment was carried out on an additional three diamonds (II*a*-5, II*a*-6, and II*a*-7) to further investigate the boundary scattering after a high vacuum anneal.

Figure 4 shows the results obtained on diamond II*a*-5 with a 4–8-μm polish (run 77) and after a high vacuum anneal at 1100 °C (run 84). The curve

TABLE II. Comparison of the slope, height of the uv tail, and color for five II*a* diamonds with polished surfaces.

Diamond	$\frac{d \log_{10} K}{d \log_{10} T}$	Height of uv tail, arbitrary units	Color
II*a*-1	2.91–2.93	0.18 ± 0.02	White
II*a*-2	2.85–2.89	0.19 ± 0.02	White
II*a*-5	2.73	0.60 ± 0.02	Brown
II*a*-6	2.83–2.88	0.28 ± 0.02	White
II*a*-7	2.87	0.20 ± 0.02	White

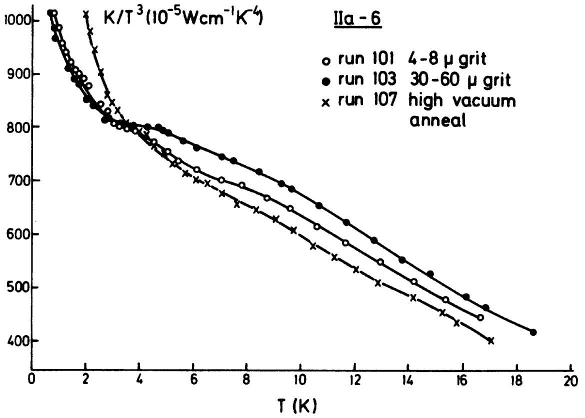

FIG. 5. Plot of K/T^3 vs T for diamond IIa-6 with three different surface treatments. The corrected theoretical Casimir value is not shown because it falls off the graph at $K/T^3 = 303 \times 10^{-5}$.

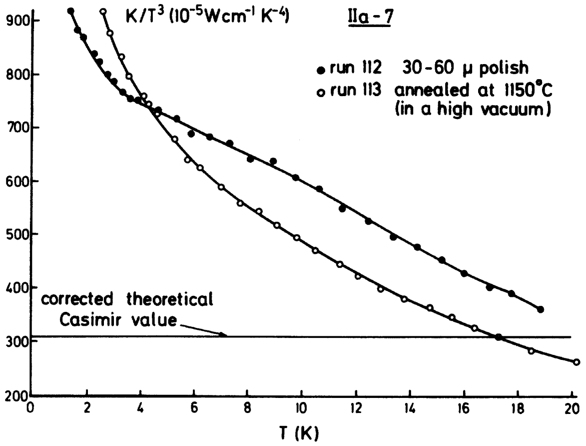

FIG. 6. Plot of K/T^3 vs T for diamond IIa-7 with a 30–60-μm polished surface and after a high vacuum anneal.

for the polished diamond shows no region where the conductivity is nearly proportional to T^3 and K/T^3 even cuts the corrected theoretical Casimir value at 16 K indicating a large amount of impurity scattering. The actual temperature dependence is $T^{2.73}$ which is considerably less than for IIa-1 and IIa-2. This difference is in agreement with the height of the uv tail. Table II shows the relationship between the slope ($d \log_{10} K / d \log_{10} T$) of the conductivity of the polished diamonds between 1 and 10 K, the height of the uv tail between 15 000 and 45 000 wave numbers and the color of the diamond. Table II clearly shows that the temperature dependence of the conductivity of polished diamonds is closer to T^3 the lower the uv tail, i.e., the purer the diamond.

The curve representing the high-vacuum-annealed diamond (run 84) crosses the curve for the polished diamond at about 3 K. Below this temperature the phonon scattering in the annealed diamond is more specular while above this temperature it is slightly more diffuse. This qualitatively agrees with the result obtained on IIa-2 [the slope of the conductivity of the annealed diamond is 2.52 (run 84) compared to 2.50 for IIa-2] but the quantitative changes are much smaller. The reason for this is that since IIa-5 is definitely not as pure as IIa-1 and IIa-2 there will be more defect scattering and less boundary scattering.

Figure 5 shows three runs on diamond IIa-6. The curve for the 4–8-μm grit polished surface (run 101) agrees with the one for the 30–60-μm polished surface (run 103) at the lowest temperatures. This is a good confirmation of the agreement between the runs on the 0–$\frac{1}{2}$- and 50-μm polished surfaces of diamonds IIa-1 and IIa-2. The K/T^3 curve for the high vacuum anneal of the 30–60-μm polished surfaces (run 107) crosses the other two runs at about 4 K in good qualitative agreement with diamonds IIa-2 and IIa-5. But again the decrease above 4 K is not as large as in run 75 (IIa-2). The slope of the conductivity of run 107 was 2.66 compared to about 2.50 for the other anneals. The slopes of the conductivity of the two polished runs were 2.83 (run 101) and 2.88 (run 103), which are about the same as for IIa-2, indicating the diamond to be quite pure. There must thus be another reason for the lack of decrease above 4 K. Two of the sides of this diamond had scratch marks running longitudinally. Instead of giving rise to diffuse scattering after the high vacuum anneal, these sides probably contributed to the specular reflection of the phonons resulting in a higher than expected K/T^3 value. Attempts to polish these two sides at 45° or 90° to the length resulted in the diamond being chipped badly making the diamond unusable for additional experiments. The diamond just would not polish in those directions (hard polishing direction).

The last experiment of this nature was done on diamond IIa-7. Figure 6 shows the K/T^3 curve for the 30–60-μm polished diamond (run 112) and the high-vacuum-annealed diamond (run 113). The latter again crosses the former at about 4 K as with all three diamonds on which this type anneal was done. The slopes were 2.87 for the conductivity of the polished diamond (run 112) and 2.63 for the annealed diamond (run 113). This change is about the same as for diamond IIa-6 but not as large as for diamond IIa-2. The direction of the scratches might play an important part in determining the conductivity after an anneal. This point would be worth a much more detailed investigation.

The runs on diamond IIa-5, IIa-6, and IIa-7 thus confirmed the results obtained on IIa-2 with a polished surface and after a high vacuum anneal but the quantitative changes were not as large. For all these diamonds it was found that after a high vacuum anneal of the diamonds with polished surfaces the conductivity was more in agreement with the height of the surface asperities than the conductivity before the anneal.

V. CONCLUDING REMARKS

Frank, Lawn, Lang, and Wilks,[22] with work on abraded (polished) diamond surfaces, showed that a polished diamond surface had a network of microcracks with an associated strain field underneath the surface. According to them the size of the cracks is of the order of the diameter of the abrading particle and the cracks lie in the $\{111\}$ cleavage planes. The side faces of the diamonds were $\{100\}$ and $\{110\}$ planes, so the cracks would be oblique to the surface. It is suggested that in the polished diamonds the phonons interact, with a nearly-frequency-independent mechanism, with this layer of cracks and its associated strain field leading to an increase of the conductivity in the boundary scattering region. The strain field would then partly or even wholly shield the surface irregularities (ridges, grooves, etc.) from the phonons. A chemical etch or a high vacuum anneal could partly or completely heal the cracks and relieve the strain field making it possible for the phonons to encounter the actual surface. This model could explain the observed results. These results would then be in some way similar to those of Worlock[10] and Thacher.[6] In their case a frequency-independent scattering mechanism off dislocations, and their associated strain fields, was suggested to explain the results (a mean free path 20% larger than the Casimir value) observed by them.

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