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LETTER TO THE EDITOR

Nitrogen in diamond: evidence from thermal conductivity

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Abstract. Measurements of the thermal conductivity of type I diamonds have been analysed in terms of various phonon-scattering processes. From the relation between the point-defect scattering rates and the total nitrogen contents, it appears that the nitrogen occurs in groups of ~ 10 atoms. The relation between nitrogen content and point-defect scattering was the same in a specimen which had a very high concentration of 'platelet' imperfections, suggesting that there is little, if any, nitrogen in the platelets. Moreover, the scattering by the platelets is ~ 50 times smaller than has been calculated on a specific model of platelets made of nitrogen.

1. Introduction

Gem-quality diamonds can be divided into types I and II on the basis of various infrared and ultraviolet absorption features. The main cause of the differences between these types is the concentration of nitrogen impurity, which is directly related to the absorption coefficient at $7.8 \mu\text{m}$. The concentration can be as high as $\frac{1}{4}\%$ in extreme type I diamonds (Kaiser and Bond 1959).

The two types can be further subdivided: type Ia diamonds contain nitrogen in such forms that it is not paramagnetic, while there is paramagnetic nitrogen in type Ib. Some type II diamonds are semiconducting—type IIb—while type IIa are not.

As type II diamonds are appreciably purer, they have the higher heat conductivity at room temperature and this is about five times greater than that of copper. The conductivities of type I diamonds range down to 'only' twice that of copper.

The aim of the present work is to relate the thermal conductivity of type I diamonds to the concentration and nature of the nitrogen and other defects, as deduced from infrared absorption and subsidiary measurements. All specimens were bars with cross section about $1 \times 1 \text{ mm}^2$ and length between 5 and 7 mm. Their conductivity was determined by the steady-state longitudinal heat-flow method between 2 and 300 K.

2. Experimental results and method of analysis

We have measured 4 type IIa specimens, 7 type Ia and 5 type Ib. Figure 1 shows some typical results; the only curves drawn are those computed in the manner to be described. Several of the curves cross because there is no relation, for different specimens, between the scattering processes which are dominant in different temperature regions. For the

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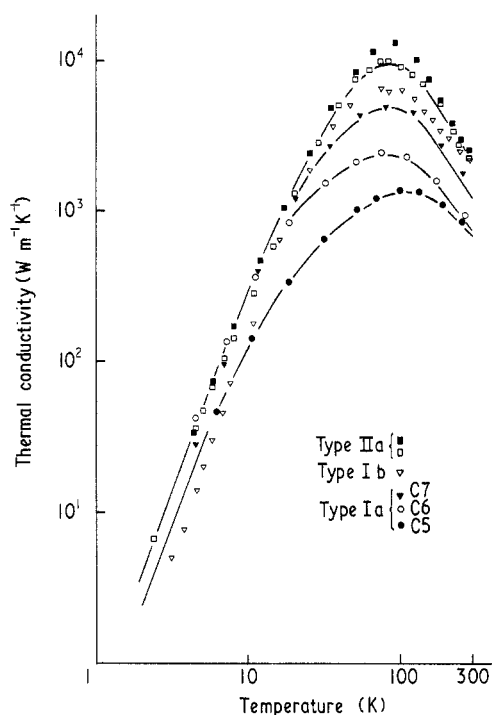


Figure 1. The thermal conductivities of representative diamonds of each of the three types measured. The curves are typical computed curves obtained in the manner described in the text.

type Ia diamonds, the nitrogen concentrations deduced from the absorption coefficient at $7.8 \mu\text{m}$ are shown in column 2 of table 1.

'Spikes' in the x-ray diffraction patterns of many diamonds have been ascribed to planar defects in the $\{100\}$ planes (Frank 1956), and platelets in these orientations were

Table 1. Information on nitrogen and on platelets in 7 type Ia diamonds, deduced from measurements of infrared absorption and thermal conductivity.

Specimen	Nitrogen concentration deduced from $7.8 \mu\text{m}$ absorption ($10^{25} \text{ atoms m}^{-3}$)	Number of nitrogen atoms in a group, n , derived from the conductivity	Absorption at $7.3 \mu\text{m}$ (100 m^{-1})	Platelet area density ($10^{22} \text{ nm}^2 \text{ m}^{-3}$)		
				From absorption coefficient	From conductivity	Stacking faults
IA-1	9	13	3.0	$\sim 10^\dagger$	0.4	1
IA-2	2	16	2.2	$< 10^\dagger$	—	—
IA-3	18	7	2.9	$\sim 10^\dagger$	0.2	1
IA-4	2	14	2.8	$\sim 10^\dagger$	—	—
C5	18	13	38	~ 500	10	200
C6	> 18	< 14	7	~ 70	1	3
C7	10	5	7	~ 80	1	3

\dagger For these low absorption coefficients, the accuracy in deriving the platelet area density is extremely poor.

seen by transmission electron microscopy by Evans and Phaal (1962). The total spike intensity correlates with the absorption at $7.3\text{ }\mu\text{m}$ (Sobolev *et al* 1968) and also with the total platelet area per unit volume (Evans and Wright 1971; see also Evans 1973). Columns 4 and 5 of table 1 give the absorption coefficients at $7.3\text{ }\mu\text{m}$ and the platelet area concentrations deduced from them (these can well be in error by a factor of 2).

The conductivity curves have been analysed by the so-called Debye expression (see, for example, Walker and Pohl 1963). It is assumed that various phonon-scattering processes act together to give a combined relaxation rate dependent on frequency, ω , and on temperature, and three-phonon normal processes are ignored (the presence of $1.1\text{ }\%$ ^{13}C ensures that there is appreciable resistive scattering at all temperatures).

The conductivity of the type IIa specimens is described by relaxation rates for Umlapp processes, and for scattering by isotopes and by a small concentration of other point defects ($\propto \omega^4$), by dislocations ($\propto \omega^1$) and by the crystal boundaries ($\propto \omega^0$). The rates for the first two are kept the same for the type I specimens, but additional scattering by point defects is required. No dislocation scattering was found necessary, while boundary scattering is dependent on surface finish and may depend on crystal orientation, so that it is adjusted for each specimen to fit the conductivity at the lowest temperatures. Most of the type Ia specimens required a relaxation rate proportional to ω^2 , which we ascribe to planar defects.

3. Type Ia diamonds

3.1. Point defects

If the additional point-defect scattering is ascribed to the nitrogen impurity, we may deduce the product of the nitrogen concentration, N , and the average number of atoms, n , in the groups into which it is arranged. The scattering cross section of a 'point' defect is proportional to the square of its volume and thus to n^2 , so that the scattering rate for a concentration c of such defects is proportional to cn^2 , which is Nn . We have derived values for Nn for each type Ia specimen, using the expression given by Turk and Klemens (1974) for the scattering by a substitutional nitrogen atom. The values for n shown in column 3 of table 1 are derived from the point-defect scattering rates which are required to fit the measured conductivity curves, on the assumption that all the nitrogen given in column 2 contributes to point-defect scattering and that the only other source of point-defect scattering is the isotopic impurity.

Some spread in the values of n might be expected from the subjectivity in judging the scattering rates which produce the best fits, but we believe that the variations we find have some significance. However, all the values are sensitive to the absolute scattering rate attributed to a nitrogen impurity. The contribution to this from the lattice strain depends on anharmonicity, and this is expressed in terms of the Grüneisen constant, γ , which we have taken as 2, following Turk and Klemens. The Grüneisen constant at normal temperatures derived from specific heat and thermal expansion is 1.1 and, if this value were more appropriate, all the n 's would be doubled.

Our range of values of n , with an average of the order of 10, agrees with $n = 8$ which was used by Turk and Klemens to fit the conductivity of a type Ia diamond measured by Slack (1973). It also agrees qualitatively with the conclusions of Davies and Summersgill (1973) that most of the nitrogen is present in small groups (they suggest 2 to 4 atoms).

3.2. Platelets

We ascribe the ω^2 relaxation rate to scattering by the platelets which appear in electron microscope pictures. At the time when Turk and Klemens started their calculations, it was generally agreed that these platelets were composed of nitrogen, and several models had been proposed for their structure. We have derived values for the platelet area per unit volume from Turk and Klemens' expression, assuming a platelet thickness of two nitrogen atoms. These values, shown in column 6 of table 1, are many times lower than those derived from the $7.3\text{ }\mu\text{m}$ absorptions, suggesting that the platelets do not scatter as strongly as assumed.

There have been suggestions recently that the platelets are not composed principally of nitrogen (Evans and Rainey 1975), or at any rate contain little of the total nitrogen in the diamond (Davies and Summersgill 1973). In view of this, we have used an expression for the scattering by a planar defect which does not involve foreign atoms, namely a stacking fault (Klemens 1957). The platelet area densities deduced from this scattering rate are given in column 7 of table 1. These are closer to the values derived from the infrared absorption, but in fact for all specimens except C5, the platelet scattering is so small that the computed conductivity is insufficiently sensitive to it for accurate scattering rates to be deduced. In addition, the $7.3\text{ }\mu\text{m}$ absorption is so small for specimens IA-1 to 4 that the platelet area concentrations cannot be deduced from it with any accuracy. Measurements on further specimens with appreciable platelet area densities will be required to show whether the moderate agreement between the two values for specimen C5 is purely fortuitous.

It should be pointed out that if the platelets *were* composed entirely of nitrogen, then in specimen C5, only 10 to 15% of the total nitrogen would be outside the platelets and thus available to scatter as point defects. The corresponding value of n in column 3 would then be 7–10 times larger. The fact that the value of n for C5 is in line with the values for other specimens (in which platelets could only account for very little of the nitrogen, even if they were composed entirely of nitrogen) provides some evidence that the platelets are *not* composed of nitrogen. Again, measurements on specimens with large platelet concentrations are required to decide whether this is a general conclusion.

4. Type Ib diamonds

The $7.8\text{ }\mu\text{m}$ absorption of all the type Ib diamonds corresponded to a total nitrogen concentration of $3 \times 10^{25}\text{ atoms m}^{-3}$ or less. The concentration of paramagnetic nitrogen can be determined separately by spin-resonance measurements and, among the specimens measured, ranged from 1×10^{23} to $1.4 \times 10^{24}\text{ atoms m}^{-3}$. The conductivities were appreciably less than that of the type IIa specimens, and from our analysis the point-defect scattering was equivalent to about 2×10^{26} single nitrogen atoms m^{-3} . Examination of two Ib diamonds by Sellschop *et al* (1974b) (see also Sellschop *et al* 1974a) showed appreciable amounts of nickel present (0.7 and 1.0 ppm). Quite apart from the scattering associated with distortion of the lattice by a nickel atom, the difference in mass between nickel and carbon is 23 times greater than between nitrogen and carbon, so that 1 ppm of nickel may well produce the same scattering as a few hundred ppm of nitrogen. One of our specimens is at present being analysed to see whether the conductivity can be explained by defects other than nitrogen.

5. Conclusions

Analysis of thermal conductivity measurements suggests that the nitrogen in type Ia specimens occurs in groups of ~ 10 atoms, and provides some evidence that the platelets seen by transmission electron microscopy are not composed mainly of nitrogen. The concentration of paramagnetic nitrogen in type Ib diamonds is not nearly enough to account for their relatively low conductivity, which must be caused by groups of nitrogen atoms and by other impurities.

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