

## Comments

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### Thermal conductivity of isotopically enriched diamonds

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The results of Anthony *et al.* [Phys. Rev. B **42**, 1104 (1990)] on the thermal conductivity at 25 °C of diamonds grown with a reduced  $^{13}\text{C}$  concentration are analyzed. The effect of reducing the  $^{13}\text{C}$  concentration is about ten times greater than these authors expected, but it is shown here that the results are not out of line with calculations made by using the variational theory of thermal resistivity, although exact predictions of the effect could not have been made prior to the measurements.

The high thermal conductivity of diamond has been an advantage in a number of its traditional uses, but has only comparatively recently found a direct application in the removal of heat from miniature electronic devices that produce heat in the process of generating electromagnetic radiation. Around room temperature the conductivity of the purest type of natural diamond (type IIa) is about 5 times greater than that of copper or silver, and this is the basis of its use as a so-called heat *sink* —it actually *conducts* heat away and does not store it (diamond's specific-heat capacity is exceptionally small). It has been known for a long time<sup>1</sup> that certainly at lower temperatures the conductivity is limited by the presence of  $^{13}\text{C}$  with a concentration  $c=1.1\%$  in natural carbon, which consists predominantly of  $^{12}\text{C}$ . This imparts an irregularity of mass throughout the crystal, leading to scattering of phonons and hence to a thermal resistivity.

It was thus of both theoretical and practical interest that Anthony *et al.*<sup>2</sup> reported on the growing of isotopically enriched diamonds and on the measurement of their thermal diffusivity at 25 °C, from which they deduced the thermal conductivity. They stated that they expected a diamond with 0.07%  $^{13}\text{C}$  to have a conductivity only about 5% greater than one with the natural isotopic constitution, but did not explain the basis of their expectation, quoting an unpublished report.<sup>3</sup> In fact, they found an enhancement of nearly 50%. In a later article<sup>4</sup> the authors of that report used an expression of Ambegaokar<sup>5</sup> for thermal resistivity due to isotopes which was deduced for "high" temperatures and was compared with results on germanium at room temperature. Although room temperature is close to the Debye characteristic temperature  $\Theta$  for Ge, it is only about  $\frac{1}{6}\Theta$  for diamond and is thus a "relatively low" temperature for it. Also, results on natural Ge were compared with those for Ge enriched to 95.8%  $^{74}\text{Ge}$ , and other work<sup>6</sup> shows that the resistivity is more sensitive to changes in  $c$  when  $c$  is small. There has recently been some correspondence<sup>7</sup> about what was

or should have been known about the effect of isotopes prior to the measurements.

Because of the small size of the specimens, a very complicated experimental method and analysis was used by Anthony *et al.*<sup>2</sup>, which could well raise doubts as to the accuracy of the results, although the value they find for diamond with the natural  $^{13}\text{C}$  content is similar to that which can be found in the literature ( $\lambda \sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$ ). At first sight the results differ qualitatively from those for LiF ( $^6\text{Li}$  and  $^7\text{Li}$ ) and He ( $^3\text{He}$  and  $^4\text{He}$ ) crystals,<sup>6,8</sup> for both of which at the same reduced temperature  $T/\Theta \sim 0.16$  hardly any effect of varying the isotope proportions is detectable for the sorts of concentrations used in the diamond measurements. This difference, however, is easily explained because in both these systems the resistivity of isotopically pure crystals is much greater than that of diamond, so that, although the calculated isotope resistivity is somewhat greater, it is estimated that in both cases the *fractional* change is only about  $\frac{1}{30}$  that produced in diamond and the 50% change in diamond would become a hardly noticeable 1–2% change in LiF and He.

The only case for which the isotope resistivity can be calculated easily, in advance of any measurements, is when the isotope concentration is small, and the only other causes of phonon scattering are three-phonon normal ( $N$ ) processes (wave vector  $\mathbf{q}$  or quasimomentum  $\hbar\mathbf{q}$  conserved), and these completely dominate the phonon distribution (i.e.,  $c \rightarrow 0$ ). Both the Ziman variational method<sup>9</sup> and Callaway relaxation-time theory<sup>10</sup> lead to the same result, which, for a crystal conforming to Debye theory, gives the thermal resistivity as

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

where  $\tau_R^{-1}(x)$  is the combined relaxation rate for resistive

processes,  $v$  is the mean phonon velocity,  $x = \hbar\omega/k_B T$ , where  $\omega$  is the angular frequency,  $2\pi\nu$ , and  $\hbar$  and  $k_B$  are the Planck constant divided by  $2\pi$  and the Boltzmann constant.

For purely mass-difference scattering by a small concentration  $c$  of an isotope differing in mass by  $\Delta M$  from the mass  $M$  of the main constituent for a crystal in which  $\omega \propto q$ ,

$$\tau^{-1}(x) = \frac{ca^3(k_B T)^4 x^4}{4\pi\hbar^4 v^3} \left[ \frac{\Delta M^2}{M} \right]^2, \quad (1)$$

where  $a^3$  is the volume per atom. For larger concentrations it must be borne in mind that both isotopes differ in mass from the mean mass  $\bar{M}$ , and the equivalent of  $c(\Delta M/M)^2$  is

$$\frac{c(\bar{M} - M_2)^2 + (1-c)(\bar{M} - M_1)^2}{(\bar{M})^2},$$

usually and here represented by  $\Gamma$ . For the case of the two carbon isotopes,

$$\Gamma = \frac{c(1-c)}{(12+c)^2}.$$

For isotope scattering, therefore,

$$W_I = \frac{\pi a^3 T}{2\hbar v^2} \Gamma \frac{J_8}{(J_4)^2},$$

where  $J_n$  is written for

$$\int_0^{\Theta/T} \frac{x^n e^x dx}{(e^x - 1)^2}$$

and for diamond at 298 K,

$$W = 2.30 \times 10^{-1} \frac{J_8}{(J_4)^2} \Gamma \text{ W}^{-1} \text{ m K},$$

for small  $c$ . The phonon density of states in diamond is very different from the  $v^2$  dependence of Debye theory, so that some effective  $\Theta$  must be used to proceed further. In the region of room temperature, the effective  $\Theta$  for the specific heat is fairly constant at  $\sim 1840$  K. We therefore take the upper limit of integration as 6.2 when  $J_8/(J_4)^2$  is 18.6, giving

$$W_I = 4.29 \Gamma \text{ W}^{-1} \text{ m K}.$$

Berman *et al.*<sup>11</sup> give a theoretical curve showing, in effect, how the actual  $W_I/\Gamma$  should differ from the limiting value when isotopes may affect the phonon distribution and lead to one that is more favorable, but the points shown there (Fig. 5), representing experimental results on many different crystals, lie below the theoretical curve. For diamond of natural isotopic composition at 298 K, the theoretical curve suggests that the limiting ( $N$  process dominant) value of  $W_I$  should be divided by about 3.5, while the experimental "curve" suggests a factor of about 1.4 (the abscissa coordinate must be shifted by the inverse reduced temperature ratio 6.2/20). The former would

give  $\lambda \sim 2700$ , the latter  $\lambda \sim 4200 \text{ W m}^{-1} \text{ K}^{-1}$  for a diamond with 0.07%  $^{13}\text{C}$ , both values representing a large enhancement. If we take the reduction factor as 2.4 ( $\pm 1$ ) for an order-of-magnitude "prediction" we obtain for an isotopically pure crystal  $W_{\Gamma=0} = 3.14 \times 10^{-10} \text{ W}^{-1} \text{ m K}$  ( $\lambda = 3200 \text{ W m}^{-1} \text{ K}^{-1}$ ). If we assume that with  $c = 0.07\%$  ( $\Gamma = 4.9 \times 10^{-6}$ ), normal ( $N$ ) processes are completely dominant, then the resistivity for this concentration should be  $W_{\Gamma=0} + 0.21 \times 10^{-4} = 3.35 \times 10^{-4} \text{ W}^{-1} \text{ m K}$  and  $\lambda \sim 3000 \text{ W m}^{-1} \text{ K}^{-1}$ , which is close to the measured value  $\lambda = 3200 \text{ W m}^{-1} \text{ K}^{-1}$ .

Rather than calculate, in this uncertain way, what the variational method might suggest for the conductivity for the other isotope concentrations, it seems more instructive to find the low-concentration form of the  $W(\Gamma)$  relation suggested by the measurements, which can then be compared with the variational and Callaway limiting form  $W_I = 4.29\Gamma$ , derived on the assumption that  $N$  processes determine the phonon distribution, so that the resistance due to umklapp ( $U$ ) processes can be regarded as a constant background, independent of  $^{13}\text{C}$  concentration.

For this purpose we could make a least-squares fit with a polynomial to all the available results. However, a three-term fit to results for LiF over the whole range of  $\Gamma$  (the conductivity at 30 K as a function of concentration is shown in Fig. 2 of Ref. 11) gives a slope at  $\Gamma = 0$  much less than a fit to only the lowest concentrations, presumably because such a simple expression does not represent well enough the whole range and does not respond sufficiently closely to the details of the low- $\Gamma$  behavior. The same holds for diamond, for which the fit to the three lowest concentrations is given by

$$W = 2.83 \times 10^{-4} + 3.61\Gamma - 1.88 \times 10^4 \Gamma^2 \text{ m K W}^{-1}.$$

The first term would be the resistivity of an isotopically pure diamond and is similar to the value previously calculated,  $W_{\Gamma=0} = 3.14 \times 10^{-4}$ . The second term is in quite good agreement with the value  $4.29\Gamma$  calculated on the assumption that  $N$  processes are dominant and that the phonon spectrum can be adequately represented by an effective Debye temperature. The expression, however, cannot represent the resistivity for  $c$  above  $\sim 1\%$  because it has a maximum at  $\Gamma \sim 10^{-4}$  ( $c \sim 1.5\%$ ) and becomes negative above  $\sim 4\%$ . As for LiF, when extending the range of  $\Gamma$  to which a polynomial is fitted, if we make a least-squares fit for all four concentrations up to 4.5%, the second term becomes much less than  $4.29\Gamma$ , namely,  $2.35\Gamma$ . Even this has a maximum for a relatively low concentration ( $\sim 6\%$ ) and is negative beyond  $c \sim 15\%$ .

We may thus conclude that the experimental results of Anthony *et al.*<sup>2</sup> on the thermal conductivity of diamonds with various  $^{13}\text{C}$  concentrations are quite in line with theory. Considering the assumptions which have to be made for a simple calculation, the low-concentration limit of the isotope resistivity, deduced from the experimental results, is in remarkably good agreement with that calculated.

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