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# Thermal Conductivity of Pure Monoisotopic Silicon

**P. G. Klemens**[1]

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The thermal conductivity of pure monoisotopic silicon is estimated by two methods, which give similar results. One estimate, based on the observed thermal conductivity of monoisotopic germanium, yields a maximum of 66 $W \cdot cm^{-1} \cdot K^{-1}$ at 22 K. The other estimate, based on measurements of natural silicon and on the theoretical isotope scattering rate, yields 75 $W \cdot cm^{-1} \cdot K^{-1}$ at 22 K, an increase of only 45% over the natural crystal. These values are for crystals of approximately 0.5 cm diameter; smaller crystals yield lower values of the maximum conductivity and smaller isotope effects. Silicon cooled to liquid hydrogen temperature seems promising for high-irradiance laser mirrors. The small gain obtained by using monoisotopic silicon would be substantially greater in cases when the generated phonon distribution is athermal and weighted to higher frequencies. The effective heat transport could then be increased by as much as a factor 60 through the use of monoisotopic silicon.

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**KEY WORDS:** heat transfer; isotopes; lasers; lattice waves; phonons; point defects; silicon; thermal conductivity.

## 1. INTRODUCTION

The lattice conductivities of crystalline insulators and intrinsic semiconductors reach their maxima at low temperatures. Near that maximum, the thermal conductivity, limited by boundary scattering and anharmonic interactions, is very sensitive to point defects, even to the mass fluctuations due to the isotopic composition. Maximizing the thermal conductivity at those temperatures requires a crystal which is not only pure and structurally perfect, but is also composed of atoms of a single isotope.

Silicon has a high thermal conductivity at low temperatures and can be readily manufactured as single crystals as well as deposited on surfaces. It

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[1] Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, USA.

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is thus of interest as a material for high-irradiance laser mirrors as well as for substrates in high-power integrated-circuit elements. It is of interest to estimate whether the heat transport properties can be significantly enhanced by using silicon crystals of a single isotope rather than silicon of natural isotopic composition. This paper estimates the maximum thermal conductivity which can be attained, and the temperature of the maximum, by using monoisotopic silicon.

The effects of isotopic composition on the low-temperature thermal conductivity have been studied experimentally for solid helium [1], lithium fluoride [2, 3], and germanium [4]. The first case differs from the others, since quantum-mechanical effects influence the stability of the lattice, and the lattice is distorted around each isotopic impurity. The studies on lithium fluoride have confirmed the theoretical model of the isotope scattering of phonons [5], particularly since the parameters describing the anharmonic interactions also fit the high-frequency ultrasonic attenuation [6]. The earliest experiment, comparing natural and monoisotopic germanium, is most relevant for the present purpose, since germanium and silicon have many similarities.

Geballe and Hull [4] found that the thermal conductivity of germanium at its maximum is higher, by a factor 3, for a monoisotopic specimen than for natural germanium. This increase, though substantial, is not as large as had been expected. This has been explained in terms of the unusual phonon dispersion of germanium. In the theoretical expression for the intrinsic thermal resistance, one must replace the Debye temperature $\theta$ by an effective value $\theta/\alpha$, which corresponds to the lowest phonon frequency at the zone boundary. Germanium, and also silicon, have each a transverse acoustic branch with a relatively low value of $\theta/\alpha$.

Two methods are used here to estimate the thermal conductivity of monoisotopic silicon. The first is simply to scale the results of monoisotopic germanium to silicon, assuming that silicon and germanium are similar in all respects except atomic mass and Debye temperature. The validity of the scaling assumption is critical for that method.

The other method relies on the existence of extensive measurements of the thermal conductivity of isotopically natural silicon, both pure and doped [7], together with Holland's detailed theoretical analysis of the thermal conductivity of silicon and germanium [8]. This analysis includes a theoretical estimate of the isotope scattering. A similar study, by Glassbrenner and Slack [9], emphasizes higher temperatures. One can then remove the isotope scattering and repeat the calculation, so as to obtain the thermal conductivity of monoisotopic silicon.

The scaling method suggests a maximum thermal conductivity of monoisotopic silicon of 66 $\mathrm{W \cdot cm^{-1} \cdot K^{-1}}$ at 22 K, compared to an observed value of 52 W · cm$^{-1}$ · K$^{-1}$ for natural silicon. In the case of germanium, the conductivity was found to increase by a factor 3 [4]. The increase of 27% estimated for silicon is smaller because the natural isotope mass variation is smaller.

The second method, that of removing the isotope scattering from the observed thermal resistance of silicon, leads to a maximum value of 75 W · cm$^{-1}$ · K$^{-1}$ at about the same temperature for monoisotopic silicon, an increase of 45% over the natural specimen. The two methods are thus in reasonable accord.

The results of both methods are size-dependent and refer to large crystals used in the measurements (about 0.5 cm in diameter). The relative change between natural and monoisotopic silicon would be somewhat less for crystals of much smaller dimensions. It is also assumed that the crystals are otherwise perfect. The difference between Holland's best sample of natural silicon (52 W · cm$^{-1}$ · K$^{-1}$) and one of Glassbrenner and Slack (35 W · cm$^{-1}$ · K$^{-1}$) show that unknown imperfections can be at least as important as isotopic composition.

## 2. SCALING FROM MONOISOTOPIC GERMANIUM

In the regime where phonon mean free paths are limited by the shortest specimen dimension $L$, the thermal conductivity is of the form [10]

$$\lambda = AT^3L/\theta^2 \tag{1}$$

where $A$ is a calculable constant and $\theta$ the Debye temperature. At low temperatures near the maximum, the mean free path due to anharmonic Umklapp processes is of the form [10]

$$1/l_u = B\left(k_B\theta/Mv^2\right)bxe^{-\theta/\alpha T} \tag{2}$$

where $B$ is a constant, $k_B$ is the Boltzmann constant, $M$ is the atomic mass, $v$ is the transverse phonon velocity, $b$ is the reciprocal lattice constant, $x = h\omega/k_BT$ is the reduced phonon frequency, and $\theta/\alpha$ is a characteristic temperature defined in terms of the lowest phonon frequency at the zone boundary ($\omega_0$) by $\hbar\omega_0 = k_B\theta/\alpha$. The constant $B$ is of order unity. It can be estimated only approximately from theory but can be deduced empirically from experimental data.

At the thermal conductivity maximum, $l_u = L$ at the reduced frequency $x = 3$. Thus from Eqs. (1) and (2), at the temperature $T_m$,

$$1/L = 3Bb(\theta/T_0)\exp\left[-\theta/\alpha T_m\right] \tag{3}$$

where $T_0 = Mv^2/k_B$, so that

$$T_m = (\theta/\alpha)/\ln(3BbL\theta/T_0) \tag{4}$$

The factors in the logarithmic term need not be estimated with high precision. For large specimens, $bL \sim 10^6$, while $\theta/T_0 \sim 10^{-2}$ and $3B \sim 1$. Thus $T_m = \theta/11\alpha$. In the case of germanium, $\theta/\alpha = 120$ K (from neutron diffraction data), so that $T_m$ should be about 11 K. The observed value is about 15 K.

Taking the thermal resistivity at the maximum to be twice the resistivity due to boundary scattering alone, it becomes

$$\lambda_m = \tfrac{1}{2} A T_m^3 L/\theta^2 \tag{5}$$

and since $T_m \propto \theta/\alpha \propto \theta$,

$$\lambda_m \propto \theta L/\left[\ln(\beta L)\right]^3 \tag{6}$$

where $\beta = 3Bb\theta/T_0$. The foregoing assumes that the similar materials germanium and silicon have the same proportionality constants, because they have identically shaped dispersion curves.

We can now estimate $\lambda_m$ of silicon from $\lambda_m$ of monoisotopic germanium. The latter has a value of 38 $\mathrm{W \cdot cm^{-1} \cdot K^{-1}}$, and since the Debye temperatures of silicon and germanium are in the ratio 1.75 : 1, we estimate $\lambda_m$ of monoisotopic silicon to be 66 $\mathrm{W \cdot cm^{-1} \cdot K^{-1}}$. With $\theta/\alpha$ for silicon being 220 K, $T_m$ should be approximately 20 K. The latter estimate is confirmed by measurements of natural silicon [7, 8], which show a peak at 22 K. Since isotopes are not expected to shift $T_m$, 22 K is our best estimate of $T_m$. In summary, the scaling of silicon from germanium indicates a maximum value of about 66 $\mathrm{W \cdot cm^{-1} \cdot K^{-1}}$ at 22 K.

## 3. CALCULATIONS FROM MEASUREMENTS OF NATURAL SILICON

Holland [8] made a detailed analysis of the thermal conductivity of natural pure silicon that accurately reproduced his experimental measurements. He used boundary scattering, estimated from first principles and confirmed by observation; isotope scattering, also estimated from theory [5], and an empirically adjusted value for anharmonic scattering, which included both normal and Umklapp processes. Though the anharmonic interaction differs from the theoretical form used in the scaling method, the functional form matters little to our calculations because we are concerned with the thermal conductivities only at one temperature.

The most obvious way of making our estimation would be to reproduce Holland's computer program and rerun it without isotope scattering. The following approximate procedure is equivalent, but less time consuming. The thermal conductivity is of the form [8]

$$\lambda \propto LT^3 \int dx\, x^4 e^x (e^x - 1)^{-2} \left[1 + ax^2 f(T) + cT^4 x^4\right]^{-1} \tag{7}$$

where $ax^2 f(T)$ is due to anharmonic processes, and $cT^4 x^4$ is due to isotope scattering. Holland calculated the relaxation rate due to isotope scattering as

$$1/\tau_{\mathrm{iso}} = 1.32 \times 10^{-45} \omega^4 \quad (\text{in } s^{-1}) \tag{8}$$

and for anharmonic processes, he found

$$1/\tau_{\mathrm{anh}} = 3.8 \times 10^{-24} \omega^2 T^3 \quad (\text{in } s^{-1}) \tag{9}$$

where $T$ is expressed in K, $\omega$ in rad · s$^{-1}$. Since $x = \hbar\omega / k_B T$, these two processes are of equal strength when

$$x^2 = 0.17T \tag{10}$$

Substituting $T_m = 22$ K for $T$, we find $x = 1.9$. At higher frequencies, isotope scattering will greatly reduce the phonon mean free path. Ignoring boundary scattering, isotope scattering will thus reduce the conductivity in the approximate ratio

$$\int_0^{1.9} j_2(x)\, dx \Big/ \int_0^{\infty} j_2(x)\, dx = 1.72/3.29 \tag{11}$$

where $j_2(x) = x^4 e^x / (e^x - 1)^2$. Values of the definite integrals are from the N.B.S. Tables of Transport Integrals [11].

The additional effect of boundary scattering can now be treated by the additive resistance approximation. The thermal resistance due to boundaries is approximately half the total resistance at the maximum. Hence,

$$W_{\mathrm{iso}} \propto (3.29)^{-1} + (1.72)^{-1} = 0.885 \tag{12}$$

and

$$W_0 \propto (3.29)^{-1} + (3.29)^{-1} = 0.608 \tag{13}$$

give the relative values of the thermal resistivity with and without isotopes, respectively. The monoisotopic sample at 22 K should therefore have a thermal conductivity larger than the pure natural sample by a factor of 1.45. Since the natural sample has a conductivity of 52 $W \cdot cm^{-1} \cdot K^{-1}$, the monoisotopic sample should have a maximum conductivity of 75 $W \cdot cm^{-1} \cdot K^{-1}$ at 22 K.

## 4. CASE OF SMALL CRYSTALS

So far we have considered crystals of relatively large dimensions ($L \sim 0.5$ cm). If $L$ is substantially reduced (say, by a factor of 10), $T_m$ increases only slightly (by a factor of 10/7) because of its logarithmic dependence on $L$, while $\lambda_m$ would be approximately 20 $W \cdot cm^{-1} \cdot K^{-1}$. The sensitivity to isotopes would diminish slightly, since $x$, the threshold frequency where point-defect scattering dominates, varies as $T^{1/2}$. We would therefore still expect almost a 20% change between natural and isotopically pure specimens. However, further reduction in size by another factor of 10 would shift $T_m$ by a factor of 1.7 to 1.8, giving $T_m = 50$ to 55 K. At that temperature, the isotope dependence would be less than 10%.

## 5. APPLICATION TO CRYOGENICALLY COOLED LASER MIRRORS

Silicon is a good heat conductor at low temperatures even in its natural isotopic form. The increase expected from monoisotopic silicon is small (25–45%) and may not be worth the additional effort except in special cases.

For maximum thermal conduction at room temperature and above, where the effect of isotopes is unimportant, it would be reasonable to choose a material with a high Debye temperature $\theta$ (low atomic mass), since the thermal conductivity at those temperatures varies as $\theta^3$. Accordingly, diamond, silicon carbide, and berylia are often considered. For conduction at low temperatures, however, a high Debye temperature is no longer advantageous. At very low temperatures, $\lambda$ varies inversely as $\theta^3$, and a low Debye temperature is preferable. Though at the conductivity maximum $\lambda$ varies roughly as $\theta$, it also varies as $L$, the smallest linear dimension of each crystal or grain. Silicon therefore has an advantage over silicon carbide or berylia simply because the crystal size can be enlarged while $\theta$ is still fairly high.

Consider a laser mirror in which the heat load to be dissipated may be as high as 100 $W \cdot cm^{-2}$ (irradiance $I = 20$ $kW \cdot cm^{-2}$ and absorptance $A = 5 \times 10^{-3}$, for example). At very low temperatures, the concept of conductivity is inappropriate because the phonons travel ballistically from surface to surface. If there is a temperature drop $\Delta T$ across two surfaces separated by distance $L$, the heat flow per unit area is $Q = \lambda \Delta T / L$. Since $\lambda$ is proportional to $L$, $Q$ is independent of $L$. An analogy is radiative heat transport between two parallel surfaces, which is also independent of the separation. However, $Q$ is proportional to $T^3 \Delta T$. The advantage of the low temperatures is that the mirror need not be particularly thin, so better provisions can be made to improve heat transfer from the solid to the cooling fluid.

The operating temperature should therefore be approximately 20 K. With a thickness of 0.5 cm and a heat current of 100 $\mathrm{W} \cdot \mathrm{cm}^{-2}$, $\Delta T$ would be approximately 1 K. That temperature drop seems quite reasonable; the real question is whether an adequate heat transfer can be made between the solid and the liquid coolant. Cryogenic liquids have less latent heat and less heat capacity than ordinary liquids, but the high thermal conductivity of the solid allows a thicker construction with wider cooling channels and more surface area.

The use of monoisotopic silicon would seem to provide only a modest advantage if it is assumed that the phonons have a thermal distribution at all points in the crystal. If, however, the losses on the reflecting surface generate extremely high frequency phonons, the picture would change radically.

Isotope scattering varies as the fourth power of frequency. The peak in the thermal energy content at temperature $T$ occurs at a frequency corresponding to $4T$. Thus at 20 K, most of the thermal energy is in the 80 K phonons, and our estimate of isotope effects is based on that assumption. If, however, the mirror surface generates mainly 220 K phonons (these modes are numerous), the isotopes would reduce the mean free path by a factor 60. This substantial reduction in heat flow could be avoided by the use of monoisotopic silicon at cryogenic temperatures.

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