Letters

Cool Diamonds

Eliot Marshall's article about General Electric's cool diamonds (News & Comment, 5 Oct., p. 25) does not discuss early work on the subject and does not point out that the results are not as unexpected as they appear to be.

I do not have first-hand familiarity with the recent history that has led to the growth of isotopically enriched carbon-12 diamond. Certainly earlier work predicted that it would have a record high thermal conductivity. In 1958, Hull and I directly measured the effects of isotopic scattering on the thermal conductivity of germanium. Credit for doing so goes back to I. Pomeranchuk in 1941 (*1*), who specifically pointed out that elastic waves suffer scattering that is proportional to the square of the mass differences of the isotopes. P. Klemens, C. Herring, and G. A. Slack contributed important analyses that are documented in our 1958 *Physical Review Letters* publication (*2*). This letter is not deeply buried, because its key result has appeared in every edition of the most widely read text in solid-state physics, Charles Kittel's *Introduction to Solid State Physics* (*3*), since the third edition in 1966. J. M. Ziman's discussion (*4*) of isotopic thermal resistance, which I believe brings out the issues very well, makes clear the uncertainties in making quantitative estimates.

At the time we did our experiment there was already strong evidence for isotopic thermal resistance. R. Berman, E. L. Foster, and J. M. Ziman at Oxford had found that over a range of temperature the exponential dependence on temperature predicted by Peierls' theory of "umklapp" scattering became suppressed as the isotopic mass variation in a variety of naturally occurring crystals became greater.

The outstanding materials capabilities and experience with germanium that existed in the research department at Bell Laboratories made it possible in 1958 to make a direct measurement of isotopic thermal resistance in germanium. We compared a crystal of 96% Ge 74 with one made from the naturally occurring isotopes and, as can be seen in Kittel's book (*3*), found an increase of more than a factor of 3 at the maximum of the thermal conductivity. This was considerably less than the factor of 15 estimated by Slack on the basis of the 15-fold decrease in the mean square deviation in isotopic mass. It is always possible near the maximum where the umklapp, boundary, and isotopic scattering processes are weak for otherwise undetectable crystalline imperfections to provide scattering that limits the conductivity. For germanium, as Conyers Herring pointed out to us, the strong dispersion of the transverse acoustical phonons, which was found almost at the same time by neutron and infrared spectroscopists, more likely provided the reason for the discrepancy. As a consequence of the dispersion, umklapp scattering occurs down to a factor of almost 4 lower in temperature in germanium than one would estimate from the Debye approximation used by the theory.

The point of the above is to provide the background for a final speculation made in our 1958 letter (*2*).

> The use of a Debye temperature in estimating umklapp-scattering is risky unless details of the vibrational spectrum are known. The data of Haynes indicate that the situation for silicon should be similar to that of germanium; furthermore the temperature dependence of the Debye theta for lead and gray tin indicates roughly a similar behavior, while that of diamond is probably more nearly normal.

If that speculation is correct, then the Debye approximation for diamond should be approximately valid. Therefore, barring residual imperfections (such as nitrogen, dislocations, and so forth), the thermal conductivity for carbon-12–enriched diamond should exceed 1000 watts per centimeter degree in the liquid nitrogen range. Present excitement comes from research (*5*) which indicates that diamond that has been largely depleted of carbon-13 has been found to be, at room temperature, a 50% better thermal conductor than any previously known material. It is even more exciting to consider possibilities at liquid nitrogen temperatures. The inexorable trend toward miniaturization of electronic components in telecommunications is limited by the extraction of heat. The use of diamond substrates in combination with hybrid semiconducting-superconducting circuits, as envisioned in the recent report of the National Commission on Superconductivity (*6*), is a worthy challenge.

It is clear that after Pomeranchuk's observation in 1941, and before 1960, knowledgeable researchers understood the physical processes underlying thermal conductivity of dielectrics and that enhancement would occur in isotopically pure diamond. What we didn't know was how to grow isotopically pure diamonds. In my opinion the credit should go to those responsible for doing it.

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REFERENCES

1. I. Pomeranchuk, *J. Phys.* **6**, 237 (1942).
2. T. H. Geballe and G. W. Hull, *Phys. Rev. Lett.* **110**, 773 (1958).
3. C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, ed. 3, 1966).
4. J. M. Ziman, *Electrons and Phonons* (Oxford Univ. Press, London, 1962).
5. T. R. Anthony *et al.*, *Phys. Rev. B* **42**, 1104 (1990).
6. *Report of the National Commission on Superconductivity* (Report to the President, National Commission on Superconductivity, Washington, DC, 7 August 1990).

Marshall's article may have left the reader with the impressions that Russell Seitz's suggestion of a high thermal conductivity of isotopically enriched diamond was original and that anybody knows how large this thermal conductivity will be. Both impressions are incorrect.

Pomeranchuk (*1*) suggested in 1942 that isotopic disorder would scatter phonons and thus reduce the thermal conductivity of dielectric crystals. Experimental evidence for the role of isotopic enrichment in increasing the thermal conductivity has thereafter been presented in several solids, for example, germanium (*2*) and lithium fluoride (*3*). In 1956, Berman, Foster, and Ziman (*4*) reported high thermal conductivities of natural diamond crystals and estimated the influence of the 1.1% concentration of carbon-13 in the carbon-12 to be potentially significant. Thus, it has been known for more than 30 years that isotopic enrichment will increase the thermal conductivity of dielectric crystals, including that of diamond. Predicting the magnitude of this increase is another matter, since the thermal conductivity of dielectric crystals is determined not only by intrinsic effects, that is, the so-called phonon-phonon scattering and the isotopic scattering. It is also influenced by any chemical or physical disorder present in real crystals. Scattering resulting from this disorder can mask the effect of the isotopes. It has been shown by Berman *et al.* (*4*) that different natural diamond crystals can have widely different thermal conductivities because of different extrinsic disorder. In any of these crystals, removal of the isotopic disorder would have a different effect. What is needed are diamond crystals with a negligible, or at least a reproducible, extrinsic disorder. Only then can we predict the effect of removing the isotopic disorder from these crystals. The remarkable achievement of the General Electric researchers is to have succeeded in growing large and apparently very perfect diamond crystals. These efforts will help us to determine the effect of the extrinsic disorder, and from that the effect of the isotopic disorder.

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REFERENCES

1. I. Pomeranchuk, *J. Phys. U.S.S.R.* **6**, 237 (1942).
2. T. H. Geballe and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).
3. R. Berman and J. C. F. Brock, *Proc. Roy. Soc. (London) A* **289**, 46 (1965).
4. R. Berman, E. L. Foster, J. M. Ziman, *ibid.* **237**, 344 (1956).

Marshall's account of how the remarkable thermal properties of monoisotopic diamond at 300 K came to light needs clarification. Between General Electric's first diamond synthesis in 1954 and my patenting carbon-12 and carbon-13 diamond in 1975, they did nothing constructive in response to early theoretical (*1–2*) or cryogenic experimental work (*3*) on the isotopic enhancement of heat conductors. Far from "hanging around their labs for years" or having "learned much of what" I know from GE, GE researchers visited me at Harvard and I visited their lab on only a few days over decades.

My years at Harvard's Gordon McKay Laboratory, like my three appointments to serve on its Faculty of Arts and Sciences, seem more germane than my lack of "degrees graduate or undergraduate" from Harvard. Thomas Anthony and Glenn Slack of GE share with me common mentors like Harvard's Nicolaas Bloembergen and Phillip Morrison at the Massachusetts Institute of Technology, whose personal knowledge of GE's arrogation of my work led them to write in protest to its directors.

Marshall quotes GE as stating that "none" of that letter's signatories "called GE to hear our side of the story." But I have learned that GE's Vice President for Research & Development, Walter Robb, called both former presidential science adviser, Jay Keyworth and MIT's Marvin Minsky months ago. Robb told Minsky GE was "bending over backwards to give [Seitz] appropriate credit."

Although GE researchers cited my work (*4*) in their recent patent disclosures, they did not cite my February 1987 MIT diamond workshop presentation "Isotopic enhancement of thermal conductivity and (laser) damage thesholds in diamond" in their recent paper "The thermal diffusivity of isotopically enriched ^{12}C diamond" (*5*), which reported the experimental confirmation of both the effects predicted in my earlier work—an improvement in thermal conductivity an order of magnitude greater than that predicted by Slack and an order-of-magnitude enhancement of the lasar damage threshold. Yet GE referred (*6*) to our differing views at a July 1987 seminar and, contrary to their denial quoted by Marshall, I did subsequently publish a paper on monoisotopic diamond and its applications (*7*).

I have recently discovered that GE was *not* the first firm to heed my admoniton to do the only thing necessary to reduce monoisotopic diamond to physical reality—just buy some purified carbon-12 or carbon-13. Without benefit of a low-pressure first-step diamond synthesis, DeBeer, Inc.'s researchers grew 0.999-pure carbon-13 diamonds from graphite in 1986 (*8*).

While Slack and other theoreticians long held that only a trivial improvement in heat conduction would occur at room temperature, I contended in my 1987 presentation that owing to diamond's remarkably high Debye temperature it could be greater than "100 WCM/°K." While it took GE a long time to empirically verify this technically important order-of-magnitude effect, its economic ramifications were quickly grasped—potential sales of $100 million a year have brought corporate lawyers into conflict with scientific ethics—any granting of credit raises the specter of compensation.

The work on the theory of conductivity done a quarter of a century or more ago deserves to be acknowledged, but GE's attempt, for apparent reasons of commercial advantage, to rewrite the more recent history of science should be rejected for what it is: an Orwellian affront to both the truth and to the honor of the scientific profession.

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REFERENCES

1. I. Pomeranchuk, *J. Phys. U.S.S.R.* **6**, 237 (1942).
2. R. Berman, E. L. Foster, J. M. Ziman, *Proc. R. Soc. Lond. A* **237**, 344 (1956).
3. T. H. Geballe and G. W. Hull, *Phys. Rev. Let.* **110**, 773 (1958).
4. R. Seitz, U.S. Patent 3,895,313, 15 July 1975.
5. T. Anthony *et al.*, *Phys. Rev. B* **42**, 1104 (1990).
6. ______, in *Synopsis of Presentations, Second Annual Diamond Technology Initiative Seminar, Durham, N.C., 7–8 July 1987* (Office of Naval Research–Strategic Defense Initiative Organization, Washington, DC, 1987), pp. 170–225.
7. R. Seitz, in *Diamond Optics, Proceedings of the Society of Photooptical Instrumentation Engineers, 16–18 August 1988*, R. Feldman and S. Holly, Eds. (Society of Photooptical Instrumentation Engineers, Bellingham, WA, 1988), vol. 969, pp. 124–137.
8. M. Seal *et al.*, European Patent Application 86304926.8 *Eur. Pat. Off. Bull.*, no. 86/52 (30 December 1986), (abandoned).

Erratum: In Jean L. Marx's Research News article "Alzheimer's pathology explored" (31 Aug., p. 984), Jie Kang, Hans-Georg Lemaire, and Benno Muller-Hill of the University of Cologne, Cologne, Germany, should have been credited for their work in cloning the gene for the amyloid protein.

Erratum: In the report "Underexpression of β cell high K_m glucose transporters in noninsulin-dependent diabetes" by J. H. Johnson *et al.* (26 Oct., p. 546), the authors' affiliations were incorrectly given. J. H. Johnson, A. Ogawa, L. Chen, T. Alam, and R. H. Unger are at the Center for Diabetes Research, University of Texas, Southwestern Medical Center, 5323 Harry Hines Boulevard, Dallas, TX 75235 and the Veterans Affairs Medical Center, Dallas, TX 75216. L. Orci is at the University of Geneva School of Medicine, 1211 Geneva 4, Switzerland. C. B. Newgard is at the Center for Diabetes Research, University of Texas, Southwestern Medical Center, Dallas, TX.