

Dresselhaus recounts work on energy-related materials

Interviewed by **Steve Yalisove**



After a postdoctoral position at Cornell University, Mildred S. Dresselhaus found a position at MIT Lincoln Laboratories where she was told to choose a field of research different from what she had been pursuing previously. “That is actually very good advice to a young person starting a career,” Dresselhaus said, “because you bring new ideas to a field that you don’t know anything about.” Dresselhaus chose fundamental studies on graphite, and carbon specifically. This was in the 1960s when virtually no one was studying this topic and, Dresselhaus said, “Graphene was just a concept.” It would be decades later before graphene would receive notice with a Nobel Prize.

MRS BULLETIN: Where do you think graphene and carbon nanotubes may have an impact in energy?

MILDRED S. DRESSELHAUS: Graphene is now very popular, yet it isn’t clear to me that graphene rather than carbon nanotubes might make it as the prime mover in energy applications or even batteries. Also, it’s very likely that the different carbon nanostructures will all have functions that will be complementary.

In the 1960s at Lincoln Laboratories, we worked on the foundations of the fundamental theory of graphite. This led to the idea that maybe we could make single layers, but we didn’t know how to do this. Along came a group at Bell Labs in the 1960s who contacted me through correspondence and encouraged me to extend the work that we had done on graphite to the intercalation compounds based on graphite. An intercalation compound is made by inserting guest species between individual layers of graphite. So you could have one graphite layer and then a guest molecule that enlarged

the layer spacing, that would be like a single layer, or you could have two layers of graphite, or three, or four, before you reached a guest molecule. The number of layers before you reached a guest species would determine what we call “the stage.” At that time, we studied experimentally and theoretically the properties of graphite intercalation compounds up to stage 11, and after that, we couldn’t keep track of what stage it was anymore. The properties didn’t change much from one stage to another beyond stage 3, so that was essentially like infinity. We studied electrical properties, optical properties, magnetic properties, you name it, everything was game at that time.

Do you think that intercalated compounds using graphite informed the people who did ion conduction of materials?

Yes. The connection between graphite and energy became apparent in 1972 to the people in industry. The first application of intercalation compounds was to battery materials because they could put ions between the graphite layers—

charge—and then the discharge was to take the charge out. Charge and discharge was just like the operation of intercalation and de-intercalation. That prompted people to study what happened to the host material when some guest species were inserted between the layers. What would it do? Would the layers just separate? How does layer 1 know that layer 6 was supposed to be intercalated next in a stage 5 compound? That was kind of a mystery to us at first. France was basically the leading country in intercalation compounds, including applications, for quite a number of years. The work led to new studies where people put a guest species in other kinds of host materials for battery and other applications. So the energy field was invigorated by these intercalation studies, and batteries became interesting in their own right independent of whether graphite was the host material.

In 1993, you published two landmark papers on the role of nanostructuring in thermoelectric materials. How did these papers come about?

I was a professor at MIT [Massachusetts Institute of Technology], and the Department of Defense visited me with representatives from both the US and French Navy. They were working together on thermoelectricity, but they didn’t yet have a program. They asked me, what are the possibilities of making thermoelectricity into a useful technology? I said I had no idea whether it was possible but let’s think about this. As you know, intercalation compounds and nanocarbon materials have thermal properties, and this seemed related to energy. I had a collaborator in this research area: Jean-Paul Issi at Louvain-la-Neuve, Belgium. We set up a meeting over there in his office, but they said, “Let’s go to a restaurant.”

So we went to a restaurant: Jean-Paul, my husband Gene Dresselhaus, the person from the French Navy, and me. Two ideas emanated from that

Steve Yalisove, University of Michigan

dinner. One, we needed to think of some new materials that were better than the materials that we currently had and that were particularly suitable for thermoelectric applications. That was Jean-Paul's role. The other idea was to study at the nano-level with the materials we already have. In the process of making nanomaterials, we learned that with the electronic density of states, the phonon electronic properties and everything change at the nano-level. So the thermoelectric properties would also be changed. I took that part of the study.

I would say that the material we use today—bismuth telluride—was discovered and developed in the 1950s. Jean-Paul tried a number of new materials; nothing really worked better at that time than those we already knew. The study on nanostructures, however, turned out to be very productive.

I had a student who was looking for a thesis topic. I said, "Let's take the simplest thermoelectric and see whether our calculation for two dimensions would indicate that it would be improved or not improved." He had the total thing worked out within a week, and we sent a manuscript to *Physical Review B*. They were happy and published it. The student wondered, "What do I do next?" I said, "Well, you did it in two dimensions. One dimension should probably work better. You should have more quantum confinement." One dimension even worked better so we wrote another paper. After that we said, "Let's figure out a material that might be good for this." Bismuth is a good thermoelectric material, and the calculations for that one turned out to be very interesting work too. We found the conditions roughly under which the real material bismuth becomes a good thermoelectric.

In fact, we are currently working on that project again now because of Dirac cones. The same linear energy-momentum relation that carbon has in the nanostructured form also can occur in bismuth-antimony alloys under certain circumstances. I would say the first three or four papers on nano-thermoelectricity in bismuth went almost unnoticed, but



all of a sudden when Dirac cones came along—pop!—there was huge interest in bismuth-related materials.

What do you think the biggest impact of nanostructuring is going to be for commercial products and thermoelectrics?

Commercial thermoelectrics are a reality. The automobile industry is now working with conventional thermoelectric materials. They are interested a little bit in nanostructuring because under some conditions, the nanostructures work.

Other discoveries have come along. One of these is recognition that the electron density of states is different in different dimensions, whether thin film, a wire, or a quantum dot. The thermoelectric properties depend directly on the density of states.

After nanostructuring, we could introduce the concept of modulation doping, which comes from semiconductor electronics. You could take advantage of the increased carrier density that's generated by certain dopants and utilize these carriers for thermoelectricity because we need to have high electrical conductivity. But we would also like to have properties like low thermal conductivity at the same time. This is very difficult to do because the Wiedemann–Franz law tells us that the electronic carriers also contribute to the thermal conductivity.

Electrons are the carriers for electricity, but they are also carriers for thermal energy. This means thermal conductivity is increased when the carrier density

is increased. To make an efficient thermoelectric material, you want to keep the electrical carrier density not too high, and for those electrons that you have, you want them to whiz through the material without getting scattered, but you *do* want the phonons to get scattered. That's what we've been working on. This is a way the research community works with people in industry: how to design material that scatters phonons without scattering electrons, and yet has high electrical conductivity but low thermal conductivity, which is difficult to achieve.

What are your views on hydrogen?

My entry into the field of hydrogen came as a great surprise. President Bush of the United States was interested in hydrogen for energy applications, and I was asked to chair a committee on hydrogen for the Department of Energy. The research that was done on hydrogen as a result of the Hydrogen Initiative has been valuable. Ultimately, maybe a hundred years from now, we expect that there'll be less oil available, the price of oil will be much higher, and hydrogen will become an increasingly important fuel for energy applications.

Energy is one topic on which different countries can work together collaboratively. If we can all produce energy from an element that's available in abundance on our planet, that would be a good thing, but we have to learn how to produce energy in large quantities, cheaply, efficiently, and without detriment to the environment. □