MATERIALS SCIENCE: Ordering Up the Minimum Thermal Conductivity of Solids

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that is quick to implement, not spatially restricted, able to assess the impacts on multiple species, and usable where existing data may be of sufficient quality or quantity. Nirvanas, even modeling ones, are the stuff of fantasy, but are there shortcuts to produce a pragmatically useful, "quick and dirty" risk-assessment approach that produces answers that are good enough? The answer, somewhat surprisingly, seems to be "yes," according to Butler *et al.* (*3*).

Like many good ideas, this approach is elegantly simple: What proportion of an organism's habitat requirements will be affected by any given environmental change? Birds inhabiting farmland require only a few types of resource: somewhere to nest, somewhere to forage in summer and winter, and food to be available in each foraging habitat. Typically, we know enough about a species' biology to estimate whether a given environmental change (e.g., a switch from spring to winter sowing) will have a negative impact on the abundance of dietary items or the amount of foraging or nesting habitats. The species' risk depends not on only the number of negative impacts but also on its specialization on the resources; this is incorporated into the risk score by a simple weighting factor. The risk score in response to six historical agricultural changes was estimated for a sample of 57 United Kingdom bird species found on farmland. This simple score is remarkably well correlated with the rate of population change over the past 40 years (and thus with the species' conservation status) and does as well as, or better than, a range of much more complex formulations.

Having developed the methodology, Butler *et al.* (*3*) illustrate its use with an assessment of how farmland birds may respond to two changes in the farmed environment. First, the widespread introduction of two species of genetically modified herbicide-tolerant crops is predicted to have little effect, a result that may contribute to public acceptance of such crops. Second, a 2005 UK agri-environment scheme offers a wide range of options, but those most commonly taken up affect the management of hedgerows and field margins. The risk assessment identifies within-crop habitat as that whose degradation most strongly affects population size. Birds' reliance on cropped areas is so strong that population declines in half to two-thirds of species will not be reversed by the widespread margin management resulting from farmers' current choices. For the scheme to reverse declines, farmers should be more strongly encouraged to take up options that address the drivers of change.

This framework not only applies to birds but also can be used on any species or groups of species whose habitat and resource requirements are known and for whom the impacts of any environmental change can be estimated. The targets could be species of conservation concern or species that provide ecosystem services (such as biocontrol or pollination), and the environmental change could be a management or a climate change. Predicting population change will always be an inexact science (*16*), but this approach is so simple that it will provide a very useful first approximation. A quick answer that is good enough may be more influential on policy than a better answer supplied years later.

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MATERIALS SCIENCE

Ordering Up the Minimum Thermal Conductivity of Solids

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Disorder usually interferes with heat conduction in most materials, but an exception has been found for insulators made from multiple layers of crystalline tungsten selenide.

Although record-high thermal conductivities in ordered materials such as diamond and carbon nanotubes have captured headlines (*1*, *2*), a few researchers have pursued materials with the minimum thermal conductivity. Although the best thermal insulators are porous (like styrofoam), many applications require electrical and mechanical properties that are only available in fully dense materials. The best nonporous insulators are amorphous dielectrics, which have conductivities as much as four orders of magnitude less than that of diamond (*3*, *4*). On page 351 of this issue, Chiritescu *et al.* (*5*) report a breakthrough value nearly an order of magnitude lower still for WSe_2 films. The material combines the thermal conductivity of a porous insulator with a density near that of copper (see the figure). In addition, the conductivity of the WSe_2 films increases after ion-irradiation damage, undermining the assumption that more disorder is better in the quest for the worst heat conductor. This finding promises improved, dense thermal insulators for gas turbine engines, thermoelectric refrigerators and power generators, and thermal data storage devices.

The highest thermal conductivity in a given material is generally achieved through crystalline order. Many of the best room-temperature heat conductors are crystals with high speeds of sound (like diamond and silicon carbide), in which atomic vibrations (phonons) carry energy hundreds of nanometers before attenuation. Ordered crystals provided early successes for the phenomenological phonon transport theory, which relates the thermal conductivity to the mean free path and heat capacity contributions of phonons [e.g., (*6*)]. Even today, with molecular dynamic simulations capturing the essential physics of conduction, phonon transport theory is helpful for interpreting the impact of localized disorder in crystals.

The minimum thermal conductivity is found in amorphous dielectrics. Atomic-scale disorder in these solids attenuates vibrational waves within a few angstroms. Con-

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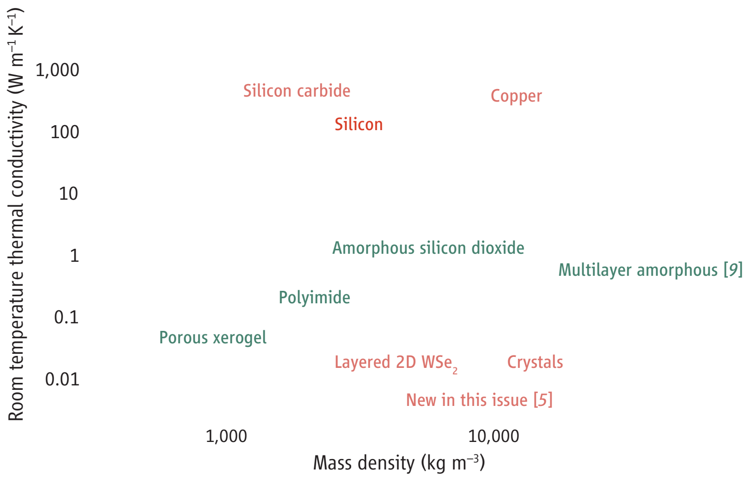

Search for the worst. Room-temperature thermal conductivities of a few representative materials compared with new data for ordered WSe_2 films (*5*). The material sets a record for the lowest thermal conductivity of a fully dense material at 300 K. Remarkably, the ultralow conductivity is achieved through the introduction of crystalline order.

ductivity modeling for amorphous materials has roots in the Einstein heat conduction model, in which atoms behave as oscillators with random phase and the vibrational attenuation length scale is near the interatomic separation. When this approach is recast with the Debye heat capacity and a mechanistic scale equal to the vibrational wavelength, conductivity predictions agree with data for a broad variety of amorphous glasses (*4*). Porosity is another route to low conductivity. Low-density xerogel films, for example, have conductivities well below 0.1 W m^{-1} K^{-1} (*7*). However, porosity strongly degrades other properties, including mechanical stiffness and electrical conductivity.

More recently, systematic layering of materials has reduced the conductivity. Material interfaces scatter atomic vibrational waves and can strongly limit the phonon mean free path. Phonon scattering at interfaces reduces the thermal conductivity and improves the thermoelectric properties (*8*). Multilayers of disordered materials lead to further conductivity reductions, with disorder and interfaces working in concert. Costescu *et al*. (*9*) showed that the thermal conductivity of disordered W/Al_2O_3 nanolaminates decreased with increasing interface density to a value of 0.5 W m^{-1} K^{-1} (see the figure).

Before the work of Chiritescu *et al*., a natural assumption was that the minimum thermal conductivity in fully dense solids would be achieved in multilayers of disordered materials. However, their results (*5*) demonstrate a dramatic further reduction in room-temperature conductivity, down to 0.05 W m^{-1} K^{-1}, in multilayers of crystalline WSe_2 sheets. The films are fabricated by depositing sequential layers of W and Se on silicon and annealing. X-ray diffraction confirms a precise layering of WSe_2 sheets with spacing of 6.6 Å, in which the crystalline orientation may be random in the direction parallel to the substrate. The thermal conductivity is measured perpendicular to the film with a well-established laser heating and thermometry technique having high sensitivity to the film properties. Although thermal conductivity data are provided only in the cross-plane direction, further research on the in-plane component is likely to capture a very large conductivity anisotropy.

The key to the low thermal conductivity lies in the WSe_2 structure, which features covalent bonding within two-dimensional sheets that are themselves bonded by weaker van der Waals forces. The authors show that the data are consistent with molecular dynamics simulations by using differing interaction energies within and between the WSe_2 sheets. The strong anisotropy of bond strengths may localize vibrational waves attempting to travel normal to the film. To confirm the connection between crystalline order and low conductivity, the authors showed that ion bombardment (and the associated disruption in the ordered *a-b* planes) increased the conductivity by a factor of 5. The conductivity increase with damage is a remarkable finding and indicates that the careful combination of order and disorder can minimize the thermal conductivity in other materials.

There is no shortage of applications for low-conductivity nonporous materials, particularly in the area of energy conversion. The challenge is to provide thermal insulators that retain other attractive mechanical, electrical, and optical properties. Thermoelectric energy conversion (refrigeration or power generation) requires low thermal conductivity, high electrical conductivity, and a high Seebeck coefficient (which relates temperature gradients and electric fields in the material). The new findings will launch research on the correct recipe of in-plane order and cross-plane disorder that impairs heat conduction while promoting electrical transport of charge and energy. Another example is thermal barrier coatings for gas turbine blades, which require thermal insulation from combusting flows (*10*). Achieving mechanical strength, high-temperature stability, and high resistance to radiative transfer will be key challenges for the new class of thermal insulators in this application. Phase change memory technology, which uses electrical current and heating to alter the stored data bits through phase transformations, has a write energy that decreases rapidly with increasing thermal resistance (*11*). The new class of thermal insulators may provide a route to minimizing the energy required for storage.

The minimum thermal conductivity is yet another example where nanostructuring enables us to reach the extreme limit of a basic material property. Because thermal conductivity is rarely the only key property, this finding highlights a challenge for nanotechnology: Nanostructured materials will find the greatest impact if they provide radically new combinations of properties, rather than merely an extreme value of one property. For applications ranging from thermoelectrics to turbine blades, the primary challenge will be to introduce the layered disorder that minimizes the thermal conductivity while maintaining the other targeted properties, including mechanical stability and high electrical conductivity.

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