

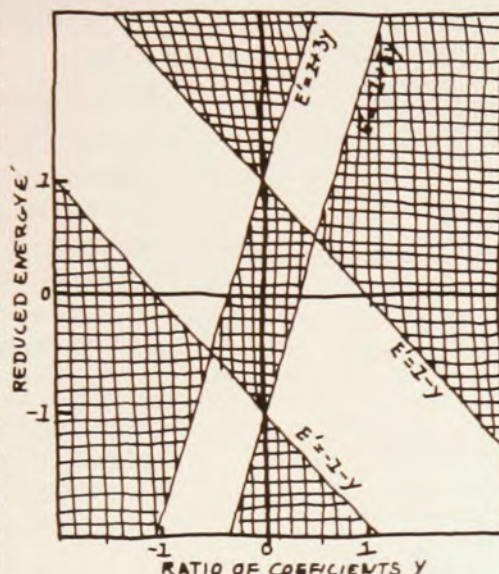
Energy gaps in amorphous materials

The "model for amorphous semiconductors," that "predicts energy band gaps" (November 1971, page 17) is not quite as new as Denis Weaire's use of it. The essential point—that the valence and conduction bands *could* be described "chemically" as combinations of bonding and antibonding orbitals respectively—was made clear, for example, by N. H. Fletcher five years ago (*Proc. Phys. Soc.* **91**, 724, 1967). The essential difficulty, which Weaire's theorem does not resolve, is to reconcile this description with the nearly-free-electron pseudopotential theory of semiconductor band structure, which also has its successes. Even in a perfect crystal the carving up of the conduction-band states into "antibonding orbitals" can only be done after one has shown that there is in fact an energy gap—thus begging the question. I agree with Weaire that the energy gap in these materials depends only on the local order; but this cannot be proved convincingly by his method. This gap between theoretical chemistry and theoretical physics can probably be bridged (see for example, T. C. McGill and J. Klima, *J. Phys. C*, **3**, L163, 1970) but it must not be papered over.

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The report on Weaire's work states that "most solid-state theorists have assumed that some kind of periodicity is needed to explain gaps," and that "previous calculations of the electronic structure of amorphous systems had added disorder to a basically periodic structure." In fact, as long ago as 1961, R. E. Borland¹ first reported a rigorous demonstration of the existence of band gaps in certain one-dimensional systems. The extension to three dimensions² was made in 1966, and is well known to workers in this field.³

Comparison of Weaire's paper with reference 2 shows that his results are simply a limiting case of the more general theorem proved earlier. In the earlier work the starting point was the



Schrödinger equation for an electron in the potential of an amorphous system, integration of which led to a relation involving the gradient of the wave function. If one replaces these gradients by the finite differences between wave functions at two discrete points one obtains Weaire's result.

References

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Focusing the light on a *bond* approach is more than welcome, because the present interest in the electronic properties of noncrystalline semiconductors is mostly centered around the band model.¹

However, the article in *PHYSICS TODAY* should have put the new results in proper perspective because the importance of short-range order in determining the properties of noncrystalline semiconductors has been long recognized.^{2,3} Although the reasoning in reference 3 is different from that in

reference 4, some of the important conclusions are the same: a forbidden band exists in noncrystalline semiconductors, and when short-range order is maintained, the forbidden band is *not* narrower than in the crystal (but departure from the long-range order makes the band edges diffuse). Furthermore, many phenomena occurring in noncrystalline solids, including glasses, semiconductors and organic polymers, have been described in terms of the basic structural units and of the chemical bonds within and between them.⁵ This approach, being essentially a chemical one, is explicitly based on short-range order.

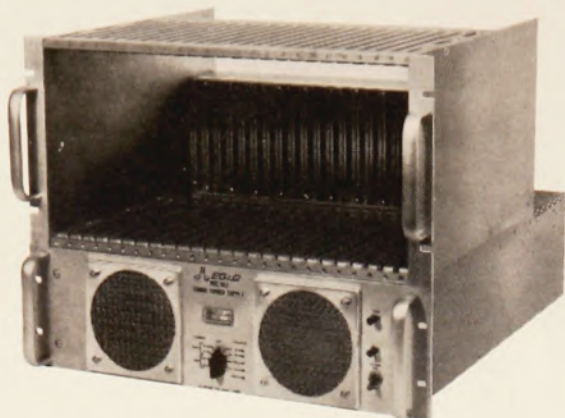
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Although we feel the news story on Weaire's theoretical prediction of sharp absorption edges in amorphous materials was a good example of timely reporting, it is worthwhile to attempt to give a clearer picture of the experimental situation in amorphous Ge. Just as in crystalline materials, sample preparation is a critical consideration in amorphous Ge. The difficulty has been that the dominant imperfection in amorphous Ge is the "microvoid,"¹ a defect uncommon in crystalline Ge. Recently sensitive techniques have been developed to detect and study the microvoids in considerable detail² and, most importantly, these tests can confirm that

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the voids have been eliminated. It has also become apparent that it is important to make samples that are defect-free as formed, rather than to try to anneal defects out after the sample has been made.

We have been able to follow the band edge as the density of these microvoids is reduced from 10% or 15% to close to zero. In this range, the band edge remains sharp but moves by tenths of an eV.³ The band gap is approximately 0.7 eV for amorphous Ge, which approaches the ideal Polk model⁴ in which all covalent bands are satisfied and no microvoids are present. By extrapolation, we suggest that the sharp edge is completely lost if the microvoid density becomes sufficiently high.

Thus, there seems to be increasingly good agreement between experiment and theory. In amorphous samples of good perfection, one has sharp edges, in agreement with Weaire; as the microvoid density is greatly increased so that the samples become much less perfect, one loses the sharp edge and finds an increased number of states in the gap, in accord with the work of Morrel Cohen.⁵ The cardinal result, though, is that the destruction of long-range order does not necessarily result in the destruction of sharp band edges.

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DENIS WEAIRE COMMENTS: John Ziman's letter appears to imply that the model that I used was such as to ascribe purely bonding and antibonding wave functions to the valence and conduction bands respectively. If such were the case, it would indeed be merely "begging the question" of the existence of a gap—but it is not the case.¹ This is not to say, however, that the question has been answered in full, as we ourselves² and others³ have repeatedly emphasized. A rigorous theoretical

demonstration of the existence of a gap in these systems, starting from something like first principles, still eludes us all. If James Phillips³ is correct in his suggestion that such an explanation will have to incorporate subtle considerations of stability, we are in for a hard time in trying to produce one. Among other things we will need much more information regarding the details of the structure, from studies of the kind that Donovan and Spicer mention, *inter alia*.

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CARLTON LOWENBERG
San Francisco

Tachyon question

Some time ago, you published a discussion of tachyons. I have a simple question about tachyons, which I have not seen discussed in print, and which might be of interest to some of your readers.

The question is: What is the form of the trajectory of a charged tachyon?

Straight-line motion at constant velocity is ruled out by momentum conservation, since Cerenkov radiation is expected. Accelerated motion along a straight line (the tacit assumption of some published discussions) is not a relativistic concept; what one observer sees as accelerated rectilinear motion will appear as curvilinear motion to

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